

Engineering Design File

Project No. 22901

V-TANK AIR STRIPPING CALCULATIONS AND PROCESS SIZING

**Idaho
Cleanup
Project**

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ENGINEERING DESIGN FILE

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5. Summary: A new characterization set for VOCs is included (provided by others, Tyson 2005). Models including concentrations and rates for the implementation of sequencing operations for the V-Tank remediation off-gas system, i.e., a roadmap, were developed showing a low sparge rate (1.5 scfm) is likely required during startup to meet a requirement of < 3 lb/hr. Mercury emissions in the off-gas were evaluated and determined to likely be speciated as mercuric chloride and relatively non-volatile at ambient conditions. Flow, PFD, material and energy balance, and pressure balance in the off-gas system were estimated based on the low sparge rate and both fans operating (e.g., 400 scfm). Information on the sparge rotameter adjustments and calibration of the photoionization detection system for VOCs is provided.				
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ACRONYMS

eV	Electron-volt
FTIR	Fourier Transform Infrared (analyzer)
GAC	Granular activated carbon
gpm	Gallon per minute
HEPA	High efficiency particulate air (filter)
PCE	Tetrachloroethylene (perchloroethylene)
PFD	Process flow diagram
PID	Photoionization detector
P&ID	Piping and instrument diagram
SCFM	Standard cubic feet per minute
STEL	Short Term Exposure Limit
SVOC	Semi-volatile organic compound
TAN	Test Area North
TFR	Technical and Functional Requirements
VOC	Volatile organic compound
WAC	Waste acceptance criteria

NOMENCLATURE^a

a	Specific surface area, L ² /L ³
A	Area, L ²
Arch	Archimedes Number
ARF	Airborne release fraction
C _i	Concentration of i in liquid, M/ L ³ or m/L ³
d _o	Orifice diameter, L
d _p	Bubble/particle diameter, L
D	Diameter, L
DF	Decontamination factor, dimensionless
D _{imp}	Impeller diameter, L
D _{iw}	Liquid diffusivity of i in water, L ² /s
D _s	Sparge ring diameter, L
D _{tk}	Tank diameter, L
E	Vapor/entrained solid, M/M
f _{oc}	Fraction organic carbon
f _{spec}	Fraction available for volatilization
F	Liquid flow rate, gpm
g	Gravity acceleration, L/t ²
g _c	Gravitational conversion, ML/F/t ²
G	Mass velocity on surface L ³ /L ² /t
H _i	Henry's Law constant of component i, FL/mol
k _D	Liquid-solid partition coefficient, L ³ /M
k _{Li}	Liquid phase mass transfer coefficient of i, L/t
k _{Lia}	Liquid phase mass transfer coefficient of I times specific surface area, t ⁻¹
k _{oc}	Organic carbon partition coefficient, L ³ /M

a. Any consistent set of units except where noted or in dimensional equations

Kow	Octanol-water partition coefficient, L ³ /M
L	Length, L
m	Mole, m
M	Mass, M
MW	Molecular weight, M/mol
no	Number of orifices
Nact	Actual impeller speed, t-1
Ni	Mass transfer flux of component i, m/L ² /t
pi	Partial pressure of i, F/L ²
P	Pressure, F/L ²
Pow_act	Actual power, LF/t
q	Concentration on GAC, M/M
Q	Gas flow rate, L ³ /t
r	Radius, L
ri	Rate, unit/t
ReG	Reynolds number, gas, dimensionless
Reo	Orifice Reynolds number
Rg	Gas constant, FL/mol/T
Rstar	Standard volume per mole of gas, L ³ /m
Sc	Schmidt number, dimensionless
Sh	Sherwood number, dimensionless
t	Time, t
Tg	Gas temperature
vg	Superficial tank velocity, L/t
vo	Orifice velocity, L/t
vs	Slip velocity, L/t
vset	Settling velocity, L/t
vt	Terminal velocity, L/t

V_g	Volume gas, L ³
V_L	Volume liquid, L ³
V_{sL}	Volume sludge, L ³
V_{tk}	Total volume, L ³
w	Gas mass flow rate, M/t
x	Horizontal distance, L
X_i	Concentration of i in solid, M/M
y, Y	Gas concentration, m/ml, ppmv, M/L ³
z_s	Fall height, L
Greek	
α, β, γ	Constants
Δ	Change in quantity
θ	Contact time, t
λ	Stripping factor based on liquids, MF/L ² /mol
Λ	Stripping factor based on solids, MF/L ² /mol
μ	Viscosity, M/L/t
μm	Micron, L
Ξ	Gassed power decision parameter
ρ_g	Gas density, M/ L ³
ρ_L	Liquid density, M/ L ³
ρ_s	Sludge density, M/ L ³
φ	Gas holdup
σ	Surface tension, F/L
τ	Residence time, t, various time constants
ω	Mass transfer rate, m/t
Ω_b	Flow regime test parameter

TANK V-14 AIR STRIPPING CALCULATIONS AND PROCESS SIZING

1. PURPOSE

This EDF provides design and modeling information to the re-design efforts of the V-Tank remediation project. There are some changes from EDF-4956, "Design for VOC Control for the TSF-09/18 V-Tank Remedial Action," (Ashworth et al. 2004a). All of the background information and model development is provided in EDF-4956. In addition, because the V-Tanks have already been transferred into the consolidation tanks, that work assumed already completed prior to this, is not in scope.

1.1 Background

See EDF-4956.

1.2 Scope

The overall project scope is to provide a treatment system for removing or minimizing the VOCs emitted from the T-Tanks during batch air-stripping (sparging). The specific scope of this EDF is to provide process design input for the treatment system. This process design includes the following:

- Present and use a new characterization set for VOCs provided by others (Tyson 2005)
- Determine appropriate models including concentrations and rates for the implementation of sequencing operations for the V-Tank remediation off-gas system, i.e., a roadmap
- Evaluate mercury emissions in the off-gas
- Provide an appropriate vacuum, flow, PFD, material and energy balance, and pressure balance in the off-gas system
- Provide limited mechanical design/unit process.

2. SAFETY CATEGORY

The safety category for the system has been designated consumer grade.

3. NATURAL HAZARDS PHENOMENA PERFORMANCE CATEGORY

N/A

4. SUBJECT-SPECIFIC DATA

4.1 Previous Work

This system was previously designed and operated. The design featured GAC beds to remove the VOCs from the off-gas. A subsequent GAC fire has resulted in this re-design effort (Ashworth et al. 2005a). The previous characterization may have underestimated the VOC content, for Tank-V9 in particular as there was not sufficient data especially in the vicinity behind the baffle where large globs of sludge resided. Also, the last operational effort included removal of the V-Tanks contents into the consolidation tanks (T-Tanks). While removing the last of the material in Tank V-9 by first pumping material and then by evaporation of excess water using air sparging, a thermal excursion in a GAC adsorption unit occurred and a melting of the GAC housing occurred in one of the parallel legs of the system from high temperature. It is now desired to operate without GAC and the new environmental release standards are based on VOC mass release rates (TFR 2005). Therefore, this EDF will limit the gas-phase VOC mass rate to: < 3 lb/hr, Emissions Regulatory Limit, < 2.5 lb/hr, Operational Limit, and < 2 lb/hr, anticipated operating condition, by adjusting the sparge air rate, using a rate controller,^b and observing the FTIR readings for total VOCs. The same correlations will be used as in the previous EDF with some updates on more accurate solid-liquid partition coefficients and better, documented entrainment correlations.

4.2 Characterization

The numbers used for modeling are taken from a recent inventory estimate of remaining quantities in the T-Tanks (derived from data leading to Tyson 2005). The values used are shown in Table 1. The concentrations, sludge mass, liquid volume, and total volume were provided. The remaining quantities in the table were calculated based on these. Depending on the use, a column for the maximum is included and an average (blended) that are used in these calculations.

Table 1. Characterization for compounds considered.

	Volumes and Concentrations: X, mg/kg, C, mg/L				
	T-1	T-2	T-3	MAX	Blended
CPCE	0.19	0.24	0.35	0.35	0.24
CTCA	2.49	2.30	5.04	5.04	2.90
CTCE	11.10	10.20	22.50	22.50	12.91
CPCB	0.02	0.03	0.01	0.03	0.02
CHg	0.03	0.07	0.06	0.07	0.05

b. The rate controller integrates flow and concentration (ppm determined via PID), shutting down sparge air if the total organic emissions exceeds 2.5 lbs in less than an hour.

Table 1. (continued).

	Volumes and Concentrations: X, mg/kg, C, mg/L				
	T-1	T-2	T-3	MAX	Blended
CCl	103.00	71.00	0.34	103.00	69.88
XPCE	712	2330	1500	2330	1415
XTCA	2930	2030	25900	25900	2533
XTCE	15100	10500	134000	134000	13100
XPCB	195	266	74	266	162
XHg	1050	1390	839	1390	872
XCl	115	191	557	557	140
XCl/XHg mol	0.62	0.77	3.74	3.74	0.90
Liquid, gal	5665	6139	2797	6139	4867
Sludge, gal	735	1061	83	1061	626
Sludge, kg	2867	4125	355	4125	2449
Volume, gal	6400	7200	2880	7200	5493
Sp.G Sludge	1.03	1.03	1.13	1.13	1.03
Gas, gal	2136	1336	5656	5656	3043
Vol%Solid	11%	15%	3%	15%	11.40%
	Mass VOCs, kg				
	T-1	T-2	T-3	MAX	Blended
PCE	1.98	9.36	0.47	9.36	4.94
TCA	8.14	8.14	8.14	8.14	8.14
TCE	42.05	42.05	42.05	42.05	42.05
Total	52.16	59.55	50.65	59.55	55.12

The characterization numbers were manipulated for model consistency when using the thermodynamic constants, H (Henry's Law constant) and k_D (the solid-liquid partition coefficient). The numbers are used in two ways in the modeling below: (1) using the sludge phase concentration, calculating the initial liquid phase based on equilibrium for the air-only model, and the gas phase based on non-equilibrium sparge relations (see Appendix B for derivations), and (2) calculating the sludge phase concentration based on the 3-phase box model, calculating the initial liquid phase based on equilibrium for the air-only model, and the gas phase based on non-equilibrium sparge relations. The following example for Methods 1 and 2 using TCE demonstrates this using the k_D and H determined from Appendix B (10.38 L/kg, 10 L-atm/mol).

Method 1 (See Table 1 for parameters and note that the blended system values are used in this EDF)

$$X_{TCE} = 13100 \text{ mg} / \text{ kg}$$

$$C_{TCE} = \frac{13100 \text{ mg} / \text{ kg}}{10.38 \text{ L} / \text{ kg}} = 1262 \text{ mg} / \text{ L}$$

$$Y_{TCE} = \frac{1.10 \text{ g} / \text{ L} * 10 \text{ L} - \text{ atm} / \text{ mol}}{131.5 \text{ g} / \text{ mol} * 0.85 \text{ atm}} * 10^6 \approx 1 \times 10^5 \text{ ppm}_v \quad P_{atm} \approx 0.85 \text{ atm}$$

The vapor concentration depends on which mode is being used. C_{TCE} exceeds the liquid concentration shown in Table 1 by a large measure, partly because the gas phase is not included. It is not believed that saturation would be the case at the start of sparging. In fact, the concentration is slightly above the solubility of TCE, 1100 mg/L (EPA 1996) and the solubility value was used to determine the equilibrium vapor concentration (Y_{TCE}). Method 1 leads to large transfer rates at very low sparge rates.

Method 2

The 3-phase box model is derived in Appendix B. The result for the sludge phase is:

$$X_i = \frac{M_i}{\left(M + \frac{V_L}{k_D} + \frac{V_{\text{gas}} \cdot R_g \cdot T_g}{k_D \cdot H_i} \right)}$$

$$X_{TCE} = \frac{42 \text{ kg}}{\left(2450 \text{ kg} + \frac{18420 \text{ L}}{10.4 \text{ L} / \text{ kg}} + \frac{11500 \text{ L} * 0.082 \text{ L} - \text{ atm} / \text{ mol} - K * 298 \text{ K}}{10.4 \text{ L} / \text{ kg} * 10 \text{ L} - \text{ atm} / \text{ mol}} \right)} = 6067 \text{ mg} / \text{ kg}$$

$$C_{TCE} = \frac{6067 \text{ mg} / \text{ kg}}{10.38 \text{ L} / \text{ kg}} = 585 \text{ mg} / \text{ L}$$

The equilibrium gas concentration is found by the Henry's Law constant:

$$Y_{TCE} = \frac{585 \text{ mg} / \text{ L}}{10^3 \text{ mg} / \text{ g} * 131.5 \text{ g} / \text{ mol}} * \frac{10 \text{ L} - \text{ atm} / \text{ mol}}{0.85 \text{ atm}} * 10^6 = 52340 \text{ ppm}_v$$

Method 1 and 2 values were both considered in this EDF using the blended system from Table 1. However, the results are only for Method 2 which are believed to be more representative during mass transfer operations (e.g., sparging). Equilibrium values for the other VOCs are included in Table 2.

Table 2. Equilibrium concentrations and parameters.

Equilibrium: 3-phase box model									
	M _i , kg	k _D , L/kg	H, L-atm/mol	MW	X _i , mg/kg	C _i , mg/L	p _i , atm	y _i , mg/L	Y _i , ppm
PCE	4.94	29.10	16.95	166	1353	46	4.75E-03	4.14E+01	5585
TCA	8.14	14.87	16.95	133.5	1694	114	1.45E-02	1.01E+02	17010
TCE	42.05	10.38	10	131.5	6062	584	4.44E-02	3.07E+02	52258
HgCl ₂	1.37	1000.00	0.16	271	324	0.32	1.92E-07	2.72E-03	0.23
PCB	1.85	208.63	0.256	327	237	1.13	8.88E-07	1.52E-02	1.04

The liquid and solid phase model non-equilibrium gas phase methods are shown below and in Appendix B. The following provides the equilibrium results based on the predicted T-Tank sludge masses.

4.3 Operational Sequencing

This item includes providing a system roadmap for operational sequencing. It provides predictions based on modeling discussed below for phases of re-starting the system. The following was determined as the sequence of events per tank:

- Slow, incremental air sparging
- Start agitators
- Start tank circulation via air pumps.

For each one of the above, a model was developed. The models are derived extensively in Appendix B. The following is a brief summary of each.

4.3.1 Step 1 – Slow, Incremental Air Sparging

The model that uses the addition of sparge air without the agitator assumes that no mass transfer from the solid occurs. This is the basic air bubbling correlation using the Sherwood number (Treybal 1987). There are a couple of assumptions that are possible within this model; constant concentration in the liquid being replenished by the solid or a falling concentration. Either of these assumptions are acceptable since the maximum gas concentrations and emission rates are used for comparison (i.e., if it dips the maximum is the same as if it's constant). The model used here is the falling concentration assumption. The Sherwood number for bubbling air is:

$$Sh = 2 + b \cdot Re_G^{0.779} \cdot Sc_L^{0.546} \cdot \left(\frac{d_p \cdot g^{0.333}}{D_L^{0.667}} \right)$$

$$k_{Li} = \frac{Sh D_{iw}}{d_p}$$

$$N_i = k_{Li}(C_i - p_i / H_i)$$

$$\omega_i = k_{Li}a(C_i - p_i / H_i)V_L$$

And for the falling concentration assumption (see Appendix B):

$$C_i(t) = C_i(0)e^{-k_{Li}a(1-\lambda_i/H_i)t}$$

Where λ is the stripping factor and provides a relation for non-equilibrium vapor phase concentrations given the assumption of high sparge/mass transfer rates:

$$\lambda_i = \frac{k_{Li}aV_L}{\omega_s / P + k_{Li}aV_L / H_i}$$

4.3.2 Step 2 – Start Agitation

The basic model for volatiles with sparge air and mixing (as developed in EDF-4956 and Appendix B) provides the change in the solid concentration as a function of time and the thermodynamic properties of the Henry's Law Constant and solid-liquid partition coefficient, the air-stripping rate and the amount of mass (both through the stripping factor):

$$X(t) = X(0)e^{-K_s^{oa}\left(1 - \frac{\Lambda k_D}{H}\right)t}$$

It is assumed that no mass of VOCs is transferred from solid to liquid during the initial sparging so that the initial concentration in the solid phase does not change during that step. The partial pressure of the volatile being derived from a mass balance with assumptions from the above is directly related to the solid concentration:

$$p(t) = \Lambda X(t)$$

4.3.3 Step 3 – Start Tank Circulation via Air Pumps

There is also a model for circulation and splashing based on Higbie's penetration mass transfer model. This is similar to the air-stripping model and is discussed in Appendix B. The circulation model used a single, equilibrium transfer unit that did not add significantly to the mass transfer. The splashing model used particles generated by circulating liquid falling approximately three feet as shown in Figure 1. The falling liquid generates small liquid bubbles as discussed in Appendix B. The generated liquid particles transfer mass via Higbie's penetration theory (Treybal 1987):

$$k_{Li} = 2\sqrt{\frac{D_{iw}}{\pi\theta}}$$

This led to a fairly high $k_L a$. However, the overall transfer is based on a small mass (the bubbles generated) and is not large compared to the air sparge or air sparge with agitation particularly at a later point in time when the concentrations are reduced. Appendix B provides the relevant information on bubble size and surface area.

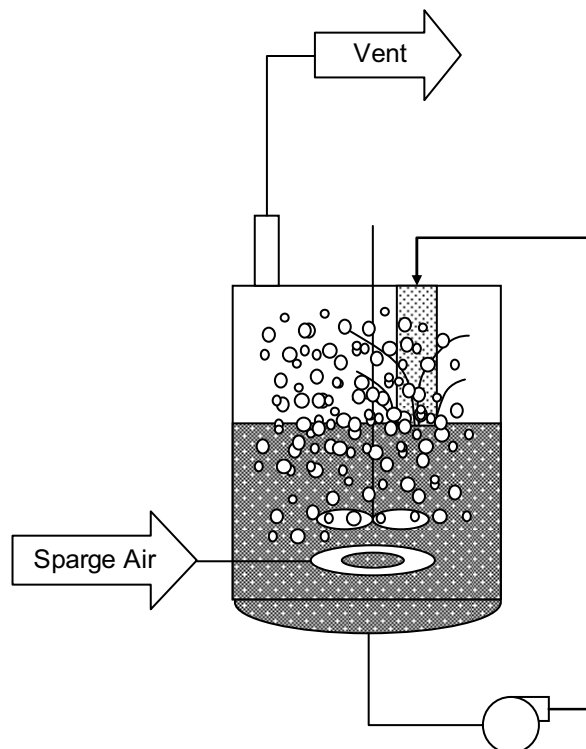


Figure 1. Circulation splash model.

4.3.4 Summary of the Models

The results of the three models are shown in Figure 2. These were based on air sparge only for five hours followed by air sparge plus agitator for an additional five hours then addition of intra-tank recirculation. It is believed that the equilibrium method (Method 2) is more accurate and 1.5 scfm can be used to start up. The characterization data used estimated masses without much regard to distribution. Therefore, the distributed method (i.e., Method 2) should be more representative during sparging. However, there is uncertainty in these numbers. The material balance (Section 4.5.3) is based on Method 2.

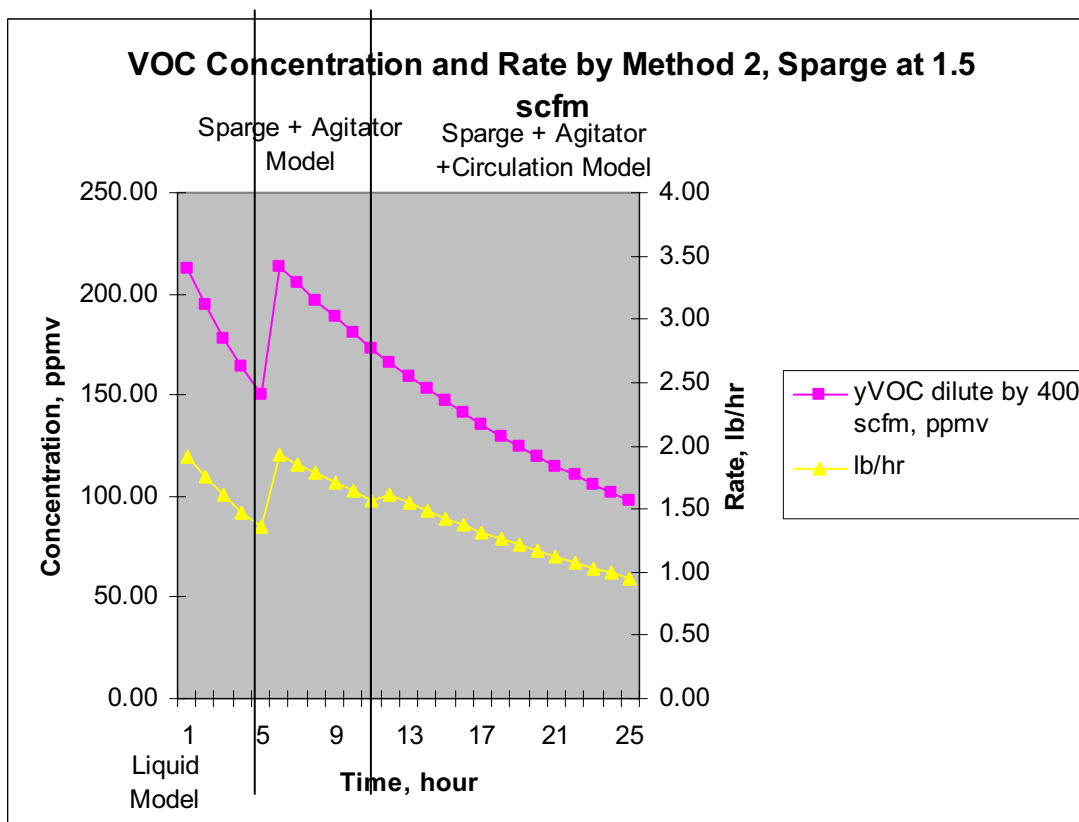


Figure 2. Concentration versus time by Method 2.

4.4 Mercury Evaluation

The above relations can be used in evaluating mercury emissions. EDF-4956 assumed the mercury was a dissolved zero-valence metal (Hg^0). Based on the characterization in EDF-4956, the chloride/mercury atomic ratio for a blended system (solids phase) is:

$$\frac{Cl}{Hg} = \frac{140 \text{ mg/kg} * 200}{872 \text{ mg/kg} * 35.5} = 0.9$$

Based on Figure 3, it is seen that there is 0.025M of volatile (available) mercury. The speciation factor is provided by the ratio of this to the peak of 0.075M, 33%. An HSC Chemistry thermodynamic modeler was used to determine species for the system. An exhaustive modeling effort for organo-mercuric compounds was not conducted. The model predicts a mixture of ionized mercury compounds (nonvolatile) HgCO_3 and HgCl_2 . The Henry's Law constants or the solid-liquid distribution coefficients for these two species are not easily found. The Henry's constant for HgCl_2 has been estimated during previous work (Ashworth 2000) on HgCl_2 as:

$$H = 0.014$$

or in units preferred in this EDF at 25°C and 0.85 atmosphere:

$$H = 0.342 \frac{L - atm}{mol} * 0.33 = 0.114 \frac{L - atm}{mol}$$

However, this is very conservative because the solid phase ratio was used. Using this and assuming a k_D of 1000^c for $HgCl_2$, the mercury emissions have been estimated based on a sparge rate of 40 cfm nominal.^d The calculations are in Appendix B. The unmitigated Hg concentration estimated from the model, maximum is 3.2 mg/m³ (undiluted with bleed air without stack dispersion factors).

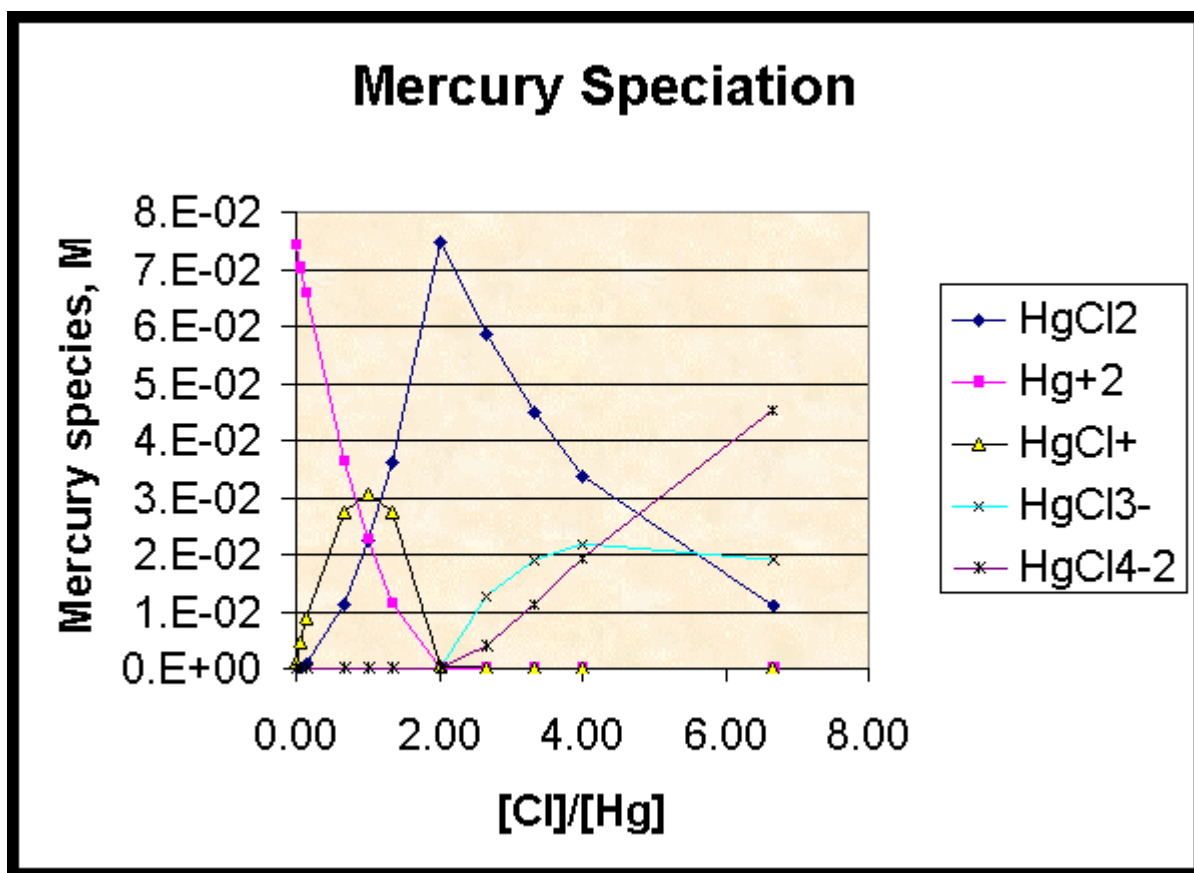


Figure 3. Speciation in Hg/Cl system.

^c. There is a lot of uncertainty in the Hg partition coefficient and the 1000 L/kg value is basically a conservative guess. The data derived from various characterization reports suggests on the order of 10,000.

^d. 40 cfm used as an upper limit based on a different end user request for Hg.

4.5 Off-gas Material and Energy Balance

4.5.1 Volatiles

Volatiles consist of the three main VOCs: PCE, TCA, and TCE. There are also some trace VOCs used for PID calibration discussed in Section 4.6.2. The total amount is controlled to less than 2.5 lb/hr by adjusting the sparge air rate. The regulatory-driven release limit is for less than 3 lb/hr for total organic release; the 2.5 lb/hr limit is a design limit that carries a safety factor for compliance. The concentrations are the upper values determined in the modeling. There may be some variation in total flow and HVAC balance will not provide exact values. Therefore, Figure 4 is provided to determine the concentrations in ppm_v versus flow. Figure 4 provides the stack flow rate on the abscissa and the diluted, total VOC concentration on the ordinate. These values were derived from the following:

$$Y_{VOC}(Q) = \frac{2 \text{ lb/hr} * 359 \text{ ft}^3 / \text{lbmol}}{166 \text{ lb} / \text{lbmol} * Q * 60 \text{ min/hr}} * 10^6$$

As long as the concentration, by the PID, is at or below the curve for whatever stack flow, the rate will be less than 2 lb/hr based on standard conditions.

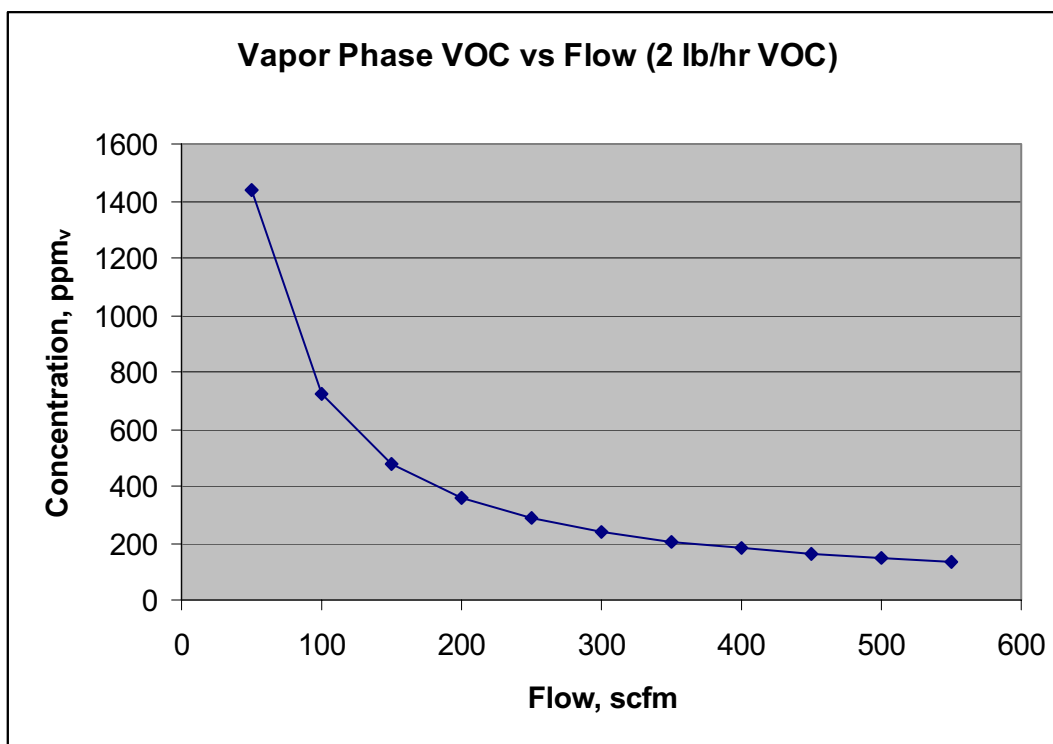


Figure 4. Allowable concentration versus total flow to meet 2 lb/hr.

4.5.2 Non-volatile Off-gas Components from Entrainment

Entrainment has been discussed in detail in the design of the current demisters that replaced the venturi/packed bed scrubber (Ashworth 2005a). The same models are used for this and the forms provided in the entrainment calculation for the PM2A Project (Ashworth 2005b).

$$E = 4 \times 10^{-6}$$

$$G_v = v \rho_g$$

$$G_d = E G_v$$

The above provides the parameters for entrainment due to sparge air introduction: the entrainment, the gas mass velocity, and the droplet mass velocity. In addition to entrainment from sparging, there is also entrainment due to splashing/spilling caused by the recirculation between the consolidation tanks. The spilling is accounted by use of the Archimedes Number:

$$\text{Arch} := \frac{\rho_g^2 \cdot z_s^3 \cdot g}{\mu_L^2}$$

$$\text{ARF} := 8.9 \cdot 10^{-10} \cdot \text{Arch}^{0.55}$$

These are used for the entrainment of radionuclides and SVOCs as shown in Appendix B.

4.5.3 Process Flow Diagram

A combination P&ID/Process Flow Diagram (PFD) is shown in Figure 5. This is based on Method 2, the equilibrium assumption for concentrations (discussed in Section 4.2). The corresponding values for temperatures, pressures, and concentrations are provided in Table 3. The VOC concentrations shown are the maximum from the three models. The PFD is based on the sparging of a single T-Tank at 1.5 scfm to start out.^e The bleed air comes in at about 400 scfm for a total of about 400 scfm.

The wet sparge air is first treated with a demister consisting of a steel mesh that removes most of the entrained particulate material. There is a low point in the line where condensation is collected prior to mixing with bleed air. Bleed air enters through a HEPA/VAC unit and mixes with wet sparge air. The mixed air is heated to prevent condensation and is sent to the stack via two parallel HEPA/VAC units.

^e. The VOCs will be slightly higher at low sparge rates prior to sparging, i.e., equilibrium.

There are two analytical devices for determining VOCs in the off-gas, a Fourier Transform Infrared Analyzer (FTIR) and a photoionization detector (PID). The FTIR has been used previously and provides near real-time (about 10 min) analysis of several VOCs. The PID has a faster response time (40 s) and measures only total VOCs. The PID has a 0-2.5 VDC analog signal such that it is used for data logging and a signal for integrating with total flow to determine the mass flow rate^f in lb/hr. They are shown wired together on the PFD/P&ID to indicate and control at 2.5 lb/hr. If the mass rate accumulates 2.5 lbs in less than one hour, the instrument signals the solenoid shown in the sparge air pipe to close, and sparging will be manually restarted at the beginning of the next hour.

The plan is to start sparging and follow the model protocol as previously discussed. After sufficient sparging at the low rate of 1.5 scfm, the sparge rate will be increased and inter-tank circulation will be started while evaluating the PID and the FTIR to ensure the VOC concentration is less than the approximate 2.5 lb/hr determined by the PID/flow integrator. For this case at 400 scfm (using 2 lb/hr), the gas phase VOC total would be about 200 ppm_v. Procedures relative to monitoring the VOC emissions and implementing sparge rate increases will be forthcoming and are beyond the scope of this EDF. However, the models provide a road map.

^f. The measurement of the instrument will actually be for ppm_v. In concert with the flowmeters, a conversion factor will be applied so the integrated total VOC flow will be expressed as pounds per hour. This is detailed in Section 4.6.2.

Table 3. Material and energy balance, two fans.

	1	2	3	4	5	6	7	8	9	10	11	12
Parameters	Sparge Air	Choked SA	T-Tank Offgas	T-Tank Comb	Bleed Air	Filtered BA	Comb Stream	Split Stream	Heated SS	Filtered SS	Compressed SS	Stack Outlet
P, psig/inH ₂ O	70	40	0.00	0.00	0.00	-3.67	-3.67	-3.67	-4.98	-5.64	0.02	0.00
T, °F	70	70	70	70	70	70	70	70	80	80	80	80
Mass Flow, lb/min	0.12	0.12	0.12	0.12	33	33	33	16	16	16	16	33
Flow, scfm	1.50	1.50	1.50	1.5	407	407	408	204	204	204	204	408
Flow, acfm	0.30	0.46	1.73	1.73	469	473	475	237	243	243	240	479
RH, %	0	0	100	100	50	50	50	50	23	23	23	23
VOCs, ppm _v	0	0	56700	56700	0	0	208	208	208	208	208	208
PCE	0	0	5300	5300	0	0	19	19	19	19	19	19
TCA	0	0	16100	16100	0	0	59	59	59	59	59	59
TCE	0	0	35300	35300	0	0	130	130	130	130	130	130
VOC, lb/hr	0	0	1.92	1.92	0.00	0.00	1.92	1	1	1	1	2
SVOCs, ppm _v												
PCB	0	0	0.7	0.7	0	0	3.E-03	3.E-03	3.E-03	3.E-03	3.E-03	3.E-03
Metals												
HgCl ₂ , mg/m ³	0	0	3.25	3.25	0	0	1.E-02	1.E-02	1.E-02	1.E-02	1.E-02	1.E-02
Radionuclides, nCi/m ³												
⁶⁰ Co	0	0	42	2	0	0	8.E-03	8.E-03	8.E-03	7.78E-05	7.78E-05	7.78E-05
⁶³ Ni	0	0	108	5	0	0	2.E-02	2.E-02	2.E-02	1.99E-04	1.99E-04	1.99E-04
¹³⁷ Cs	0	0	790	40	0	0	1.E-01	1.E-01	1.E-01	1.45E-03	1.45E-03	1.45E-03

Further modeling has been conducted to show changes in parameters with sparge rate (Lopez 2005). These ranges are shown in Table 4.

Table 4. Flow ranges and parameters.

Sparge Rate	Expected Bleed Air Flow Reading on FIT-1 (SCFM)	Expected Total Flow Reading on FIT-2 (SCFM)	Expected Vacuum Reading on PIS-1 (IWG)	Expected Vacuum In Tanks Being Sparged (IWG)
1.5 SCFM in 2 Tanks ^g	385 TO 460	390 TO 465	-2.9 TO -3.8	-2.9 TO -3.8
5 SCFM in 2 Tanks ^h	380 TO 455	390 TO 470	-2.7 TO -3.7	-2.7 TO -3.8
10 SCFM in 2 Tanks	380 TO 450	400 TO 470	-2.7 TO -3.7	-2.7 TO -3.7
20 SCFM in 2 Tanks	370 TO 440	410 TO 480	-2.5 TO -3.4	-2.6 TO -3.5
30 SCFM in 2 Tanks	365 TO 430	425 TO 490	-2.3 TO -3.2	-2.5 TO -3.4
40 SCFM in 2 Tanks	355 TO 420	435 TO 500	-2.0 TO -2.8	-2.4 TO -3.2
1.5 SCFM in 3 Tanks ^g	385 TO 460	390 TO 465	-2.9 TO -3.8	-2.9 TO -3.8
5 SCFM in 3 Tanks ^h	380 TO 455	395 TO 470	-2.8 TO -3.8	-2.8 TO -3.8
10 SCFM in 3 Tanks	375 TO 445	405 TO 475	-2.7 TO -3.5	-2.7 TO -3.6
20 SCFM in 3 Tanks	365 TO 430	425 TO 490	-2.4 TO -3.3	-2.5 TO -3.4
30 SCFM in 3 Tanks	350 TO 415	440 TO 505	-2.1 TO -3.0	-2.3 TO -3.2
40 SCFM in 3 Tanks	340 TO 395	460 TO 515	-1.8 TO -2.6	-2.1 TO -2.9

g. 90 SCFH

h. 300 SCFH

4.6 Design and Operating Features

4.6.1 Sparge Air Rotameters

To record data and monitor the flow of sparge air, a correction factor is required for the sparge air rotameters, V-TANK-REM-ROT-1, -2, -3. The correction is to standard conditions defined as $T = 460^{\circ}R$ ($273.3^{\circ}K$) and $P = 14.7$ psi (1 atm). The correction is (Dwyer 2004):

$$Q_S = Q_{rot} \sqrt{\frac{P_{rot} T_S}{P_S T_{rot}}}$$

Example, $P_{rot} = 40$ psig, $T_{rot} = 55^{\circ}F$, $Q_{rot} = 20$ cfm:

$$Q_S = 20 \text{ cfm} \sqrt{\frac{(40 \text{ psi} + 14.7 \text{ psi}) 460^{\circ}R}{14.7 \text{ psi} (460^{\circ}R + 55^{\circ}F)}} = 36.5 \text{ scfm}$$

Table 5 is provided for various temperatures and pressures.

Table 5. Rotameter corrections.

P, psig	20	20	20	30	30	30	40	40	40	50	50	50	60	60	60	70	70	70	80	80	80
T, °F	40	60	80	40	60	80	40	60	80	40	60	80	40	60	80	40	60	80	40	60	80
Q _{rot} , cfm	Q _S , scfm																				
1	1.5	1.4	1.4	1.7	1.6	1.6	1.9	1.8	1.8	2.0	2.0	1.9	2.2	2.1	2.1	2.3	2.3	2.2	2.4	2.4	2.3
2	2.9	2.9	2.8	3.3	3.3	3.2	3.7	3.6	3.6	4.0	3.9	3.9	4.3	4.2	4.2	4.6	4.5	4.4	4.9	4.8	4.7
4	5.9	5.8	5.7	6.7	6.6	6.4	7.4	7.3	7.1	8.0	7.9	7.7	8.6	8.5	8.3	9.2	9.0	8.9	9.7	9.5	9.4
6	8.8	8.7	8.5	10.0	9.8	9.7	11.1	10.9	10.7	12.1	11.8	11.6	13.0	12.7	12.5	13.8	13.5	13.3	14.6	14.3	14.1
8	11.8	11.6	11.3	13.4	13.1	12.9	14.8	14.5	14.2	16.1	15.8	15.5	17.3	17.0	16.6	18.4	18.1	17.7	19.5	19.1	18.7
10	14.7	14.5	14.2	16.7	16.4	16.1	18.5	18.1	17.8	20.1	19.7	19.4	21.6	21.2	20.8	23.0	22.6	22.2	24.3	23.9	23.4
12	17.7	17.3	17.0	20.1	19.7	19.3	22.2	21.8	21.4	24.1	23.7	23.2	25.9	25.4	25.0	27.6	27.1	26.6	29.2	28.6	28.1
14	20.6	20.2	19.9	23.4	23.0	22.5	25.9	25.4	24.9	28.2	27.6	27.1	30.3	29.7	29.1	32.2	31.6	31.0	34.1	33.4	32.8
16	23.6	23.1	22.7	26.8	26.2	25.8	29.6	29.0	28.5	32.2	31.6	31.0	34.6	33.9	33.3	36.8	36.1	35.4	39.0	38.2	37.5
18	26.5	26.0	25.5	30.1	29.5	29.0	33.3	32.7	32.0	36.2	35.5	34.9	38.9	38.2	37.5	41.4	40.6	39.9	43.8	43.0	42.2
20	29.5	28.9	28.4	33.5	32.8	32.2	37.0	36.3	35.6	40.2	39.5	38.7	43.2	42.4	41.6	46.0	45.2	44.3	48.7	47.7	46.9
22	32.4	31.8	31.2	36.8	36.1	35.4	40.7	39.9	39.2	44.3	43.4	42.6	47.6	46.6	45.8	50.7	49.7	48.7	53.6	52.5	51.5
24	35.4	34.7	34.0	40.1	39.4	38.6	44.4	43.5	42.7	48.3	47.4	46.5	51.9	50.9	49.9	55.3	54.2	53.2	58.4	57.3	56.2
26	38.3	37.6	36.9	43.5	42.6	41.8	48.1	47.2	46.3	52.3	51.3	50.3	56.2	55.1	54.1	59.9	58.7	57.6	63.3	62.1	60.9
28	41.3	40.5	39.7	46.8	45.9	45.1	51.8	50.8	49.9	56.3	55.2	54.2	60.5	59.4	58.3	64.5	63.2	62.0	68.2	66.8	65.6
30	44.2	43.4	42.5	50.2	49.2	48.3	55.5	54.4	53.4	60.4	59.2	58.1	64.9	63.6	62.4	69.1	67.7	66.5	73.0	71.6	70.3
32	47.2	46.2	45.4	53.5	52.5	51.5	59.2	58.1	57.0	64.4	63.1	62.0	69.2	67.8	66.6	73.7	72.2	70.9	77.9	76.4	75.0
34	50.1	49.1	48.2	56.9	55.8	54.7	62.9	61.7	60.5	68.4	67.1	65.8	73.5	72.1	70.7	78.3	76.8	75.3	82.8	81.2	79.6
36	53.1	52.0	51.0	60.2	59.0	57.9	66.6	65.3	64.1	72.4	71.0	69.7	77.8	76.3	74.9	82.9	81.3	79.8	87.6	85.9	84.3
38	56.0	54.9	53.9	63.6	62.3	61.2	70.3	68.9	67.7	76.5	75.0	73.6	82.2	80.6	79.1	87.5	85.8	84.2	92.5	90.7	89.0
40	58.9	57.8	56.7	66.9	65.6	64.4	74.0	72.6	71.2	80.5	78.9	77.5	86.5	84.8	83.2	92.1	90.3	88.6	97.4	95.5	93.7

If the actual flow and the real velocity are desired, the following is used assuming the ideal gas law and the local atmospheric pressure (P_a) is 0.85 atm:

$$Q_a = Q_s \frac{P_s}{P_a}$$

4.6.2 VOC Analyzer/Mass Totalizer

A RAEGuard PID will be used to analyze and indicate total VOCs. The scale for the PID needs to match the expectation value for meeting the 2 lb/hr criterion. Assuming 400 scfm to determine the scale for the PID, the total VOC assuming a conservative molecular weight of 166 g/mol for PCE, the concentration is:

$$VOC = \frac{2lb/hr * 359 ft^3 / lbmol}{400 ft^3 / min * 166 lb / lbmol * 60 min / hr} * 10^6 = 180 ppm_v$$

Therefore, the scale will be 0-1000 ppmv.

The PID will be integrated with the flowmeter, V-TANK-REM-FIT-2, to obtain the rate in lb/hr by a multiplying operator function, i.e.:

$$lbVOC/hr = ppm_v * scfm * \left(\frac{1}{10^6} * \frac{60 min}{hr} * \frac{lbmol}{359 ft^3} * \frac{134 lb}{lbmol} \right) * 1.27 = ppm_v * scfm * 2.84 \times 10^{-5}$$

The multiplication operator for the instrument is then 2.84×10^{-5} . The factor of 1.27 in the above is the f_G from Appendix B. Appendix B provides details concerning this and methods of changing it if the FTIR data indicate significant variations from the basis mole fractions, especially TCA that has a relatively high CF. The factor f_G is referred to as an exterior factor whereas the PID correction factors are entered directly into the PID. To summarize, the mixture correction factor is determined based on the individual correction factors from the vendor at the PID lamp power used (in this case 10.6 eV) and the mole fractions of the gas-free VOCs (i.e., mole fractions based only on VOCs).

$$CF_{mix} = \sum_{i=1}^n \frac{1}{\frac{x_i}{CF_i}}$$

The mixture correction factor (CF_{mix}) is 0.55 from Appendix B. It is recommended to leave the humidity correction factor at 1.0 unless the humidity is consistently higher than about 20% as shown in the humidity correction plot, Figure 6. A simplified sketch for the integrator instrument is shown in Figure 7.

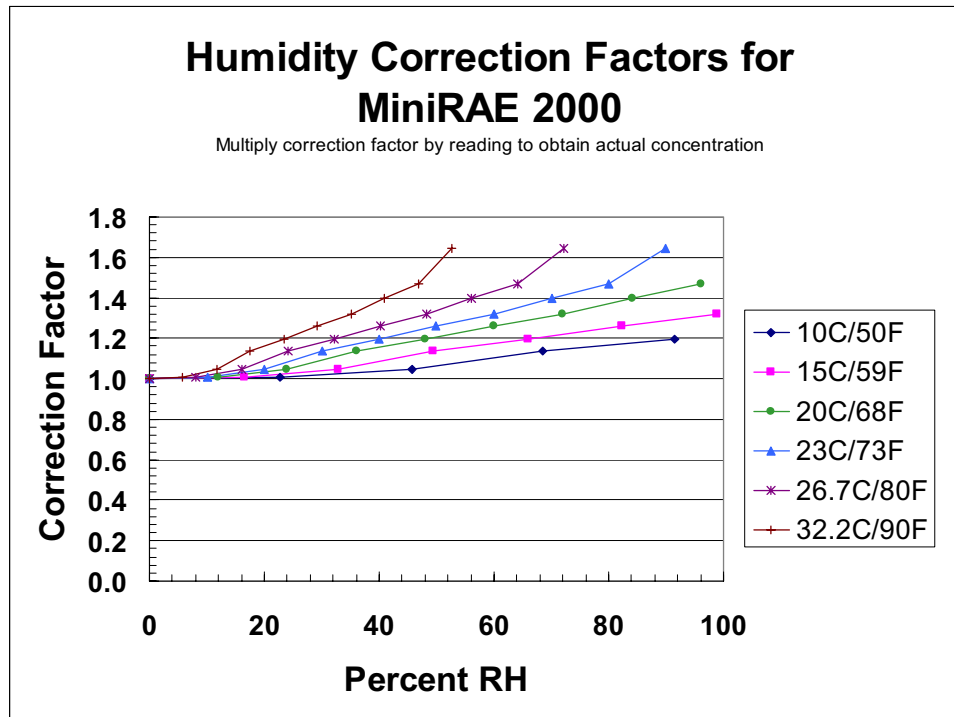


Figure 6. Humidity correction factor.

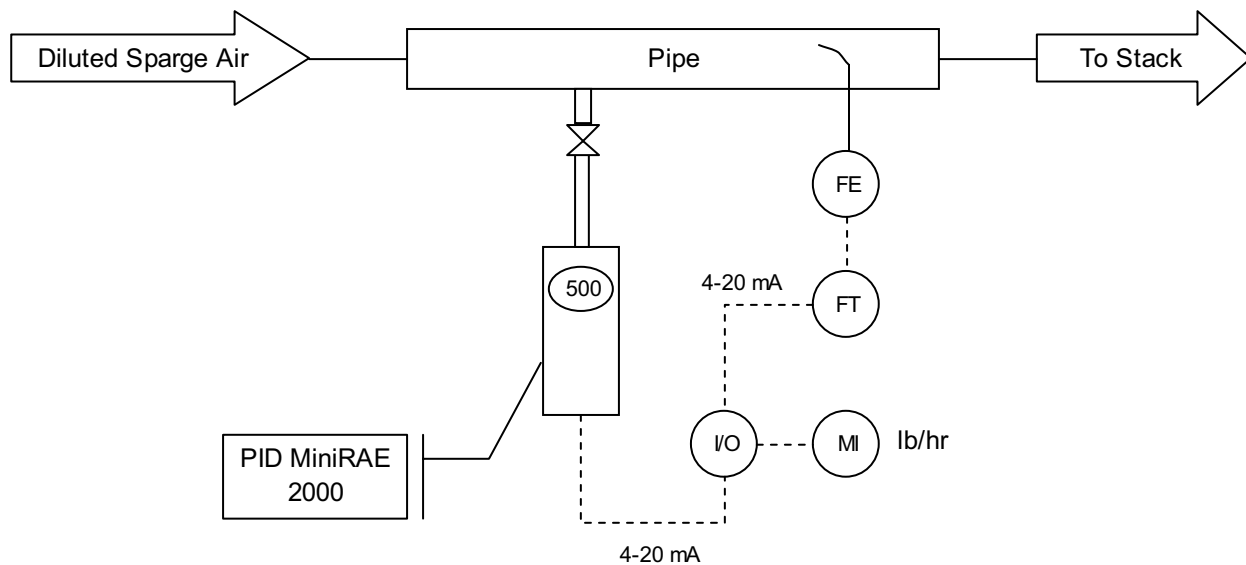


Figure 7. Simplified VOC mass flow instrument.

5. ASSUMPTIONS/UNCERTAINTIES

- Without sampling, there is uncertainty in the solid, liquid, and gas concentrations. The model used two methods to help bracket this.
- The mass transfer model for sparge air coupled with the agitator is not known to be applicable at low sparge rates. Therefore, that model could be less accurate at low flow.
- The recirculation modeling is very difficult to formulate and could be less accurate depending on the recirculation flow that was assumed 100 gpm.
- The mercury was assumed to be speciated as chloride complexes. No thermodynamic modeling was done for possible organo-mercuric compounds.
- Assumed no mass transfer from solid during liquid model (sparge only). Also used the decaying liquid concentration. It could be more of a constant but should not matter since the highest of all gas phase concentrations are put in flowsheet.

6. ACCEPTANCE CRITERIA

The total VOC emissions must be < 3 lb/hr, Emissions Regulatory Limit, < 2.5 lb/hr, Operational Limit, and < 2 lb/hr, anticipated operating condition, per project instructions. The operating sequence discussed in this EDF provides a roadmap for operating the redesigned off gas system in compliance with these emission limits. The off gas volatile organic monitoring and control system provides a means to provide emission rate feedback to operations and controls sparge air supply to ensure the regulatory limit is not exceeded.

Technical and Functional Requirements (ICP 2005), relevant to this EDF, and how they are met are provided in Table 6.

Table 6. Technical and Functional Requirements matrix.

Requirement	Design to Meet
3.1.2.5-1. The off-gas system design shall provide ventilation capability to ensure the volatile organic compounds (VOCs) and particulate radionuclides are not released above allowed levels to the atmosphere during the waste transfer/consolidation process.	Instrumentation has been included to allow monitoring and control of the VOC rate in lb/hr. Demisters and HEPAs are provided. However, these were not designed to meet an allowed level.
3.1.2.5-2. The off-gas system design shall provide ventilation capability and sparging controls to enable operations to ensure VOCs are not released above allowed levels (3 lbs per hour) to the atmosphere during the waste sparging process.	The design provides a demister and HEPAs and monitoring/control for the 3 lb/hr VOC requirement. It also provides ability to startup at low sparge rates.
3.1.2.5-4. The off-gas system shall prevent radionuclide and toxic emissions to an on-site worker in accordance with 40 CFR 61.92 and DOE 5400.5, "Radiation Protection of the Public and the Environment."	Instrumentation has been included to allow monitoring and control of the VOC rate in lb/hr. Demisters and HEPAs are provided. However, it does not evaluate or provide design media showing levels to on-site workers. See EDF-6327
3.1.2.5-5. The off-gas system shall be designed to allow sampling/measuring for potential releases of hazardous and radioactive effluents to the environment, as required by the Air Permit Application Determination.	Instrumentation and sample ports are provided to measure VOCs and radionuclides.
3.1.2.5-6. The off-gas system shall be designed to ensure releases of radioactive materials to the environment and community are within acceptable limits (10 mrem/yr for the off-Site receptor) as defined by 40 CFR 61, "National Emission Standards for Hazardous Air Pollutants," Subpart H, "National Emission Standards for Emissions of Radionuclides Other Than Radon from Department of Energy Facilities."	The design provides a demister and HEPAs. However, it does not evaluate or provide design media showing any dose rate to the environment or community. See EDF-6332
3.1.2.5-7. The design process shall include appropriate controls and monitoring equipment for carcinogenic and noncarcinogenic contaminants, which may be released into the air.	There is not a breakdown of carcinogenic and noncarcinogenic contaminants in this design or any evaluation of this. This design only provides for monitoring VOCs to help control the total rate to < 3 lb/hr. Instrumentation and sample ports are provided to measure VOCs and radionuclides.
3.1.2.5-8. The off-gas system shall be designed to ensure the integrity of the in-line HEPA filters is maintained.	Preheaters are provided to prevent condensation.
3.1.2.5-9. The off-gas system shall be designed to have sufficient flow capacity to accommodate sparging the consolidation tanks.	The flow capacity of sparging all three tanks is exceeded by two fans in parallel.
3.1.2.5-10. The off-gas system shall be designed such that the relative humidity is less than 80% and the temperature is less than 50°C (122°F) when the off-gas enters the HEPA filters.	Preheaters are provided that will reduce the RH to < 80%.
3.1.2.5-11. The off-gas system shall be designed such that off-gas condensate is minimized and any condensate that is removed by the off gas system can be returned to the consolidation tanks.	Condensate removal system provided.

Table 6. (continued).

Requirement	Design to Meet
3.1.2.5-12. The off-gas system design shall provide capability to measure the pressure drop across the HEPA filters.	Pressure drop gauges provided.
3.1.3.2. The consolidation tank and off-gas systems shall be designed to readily interface with the Phase II treatment system.	Not addressed by this EDF.
3.1.4 Codes and Standards	Not all examined for appropriateness.
3.2.2.3. The design shall be protective against human overexposure to radiation, airborne radionuclides, and hazardous chemicals during the project operations.	The design provides a demister and HEPAs and monitoring/control for the 3 lb/hr VOC requirement. However, it does not evaluate or provide design media showing protectiveness or lack thereof. See EDF-6327
3.3.5-1. The design shall include process control and monitoring instrumentation for all critical process parameters.	VOC monitoring is conducted with an in-line PID with verification monitoring by FTIR.
3.3.5-2. The design shall ensure that control sensors within the design determined to be critical to successful operation, are redundant.	None identified.
3.4.1-1. The project design shall provide features (e.g., attributes and components) in the transfer and consolidation systems that facilitate leak and pressure testing.	No specific design media for this other than standard features.
3.4.1-2. The project design shall provide features in the off-gas systems that facilitate testing for operability.	No specific design media for this other than standard features.

7. SOFTWARE

The following industry-wide software, requiring no validation, was used for this EDF:

- Mathcad Version 11
- EXCEL Version 2003.

8. CALCULATIONS

See Appendix B.

9. CONCLUSIONS

It is concluded that the system can be operated to maintain less than 2 lb/hr. However, the sparge rate is low starting out. It is not expected to require a very long time even at low sparge rates but the rates need to be increased as long as the VOC rate is about 2 lb/hr, an anticipated operating rate established by project management to ensure compliance of the regulatory emissions limit of 3 lb/hr.

10. RECOMMENDATIONS

The modeling provides insight that at low sparge rates, the driving force decreases so that the mass rates become vanishingly small so that sparge rates need to be increased. Also see body of EDF for specific actions.

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Appendix A

Task Planning Documentation

APPENDIX A

Task Planning Documentation

The task planning document is covered in the Work Agreement (Work Agreement 2005).

Appendix B

Calculations

Appendix B

Calculations for V-Tank Remediation Redesign

Table of Contents

- I. Data
- II. Models for scope of effort
- III. Flowsheet and HVAC Balance
- IV. VOC Analyzer

I. DATA

Temperature and Pressure

$$T_g := 298K \quad P := 0.85atm$$

Gas constants

Standard gas per mole of substance

$$R_g := 0.08205 \frac{L \cdot atm}{mol \cdot K} \quad R_{star} := \frac{R_g \cdot 273.16K}{1atm} \quad R_{star} = 22.413 \frac{L}{mol}$$

Derived Units/Miscellaneous

$$Ci := 3.7 \cdot 10^{10} s^{-1} \quad \text{Curie definition} \quad nCi := 10^{-9} Ci$$

$$ppm_v := \frac{atm}{atm} \cdot 10^{-6} \quad lbmol := 454mol$$

Volumes, masses, concentrations

The table from the body is put in data form below to make use of as values.

DATA :=	0	"T-1"	"T-2"	"T-3"	"MAX"	"Blended"
	"CPCE"	0.19	0.24	0.35	0.35	0.24
	"CTCA"	2.49	2.30	5.04	5.04	2.90
	"CTCE"	11.10	10.20	22.50	22.50	12.91
	"CPCB"	0.02	0.03	0.01	0.03	0.02
	"CHg"	0.03	0.07	0.06	0.07	0.05
	"CCI"	103.00	71.00	0.34	103.00	69.88
	"XPCE"	712	2330	1500	2330	1415
	"XTCA"	2930	2030	25900	25900	2533
	"XTCE"	15100	10500	134000	134000	13100
	"XPCB"	195	266	74	266	162
	"XHg"	1050	1390	839	1390	872
	"XCI"	115	191	557	557	140
	"XCI/XHg mol"	0.62	0.77	3.74	3.74	0.90
	"Liquid, gal"	5665	6139	2797	6139	4867
	"Sludge, gal"	735	1061	83	1061	626
	"Sludge, kg"	2867	4125	355	4125	2449
	"Volume, gal"	6400	7200	2880	7200	5493
	"Sp.G Sludge"	1.03	1.03	1.13	1.13	1.03
	"Gas, gal"	2136	1336	5656	5656	3043
	"Vol%Solid"	"11%"	"15%"	"3%"	"15%"	"11.40%"
	"Mass VOCs, kg"	0	0	0	0	0
	"PCE"	1.98	9.36	0.47	9.36	4.94
	"TCA"	8.14	8.14	8.14	8.14	8.14
	"TCE"	42.05	42.05	42.05	42.05	42.05
	"Total"	52.16	59.55	50.65	59.55	55.12
	"Mass HgCl2 and PCB, kg total"	0	0	0	0	0
	"HgCl2"	9.04	0	0	0	3.01
	"PCB"	0.77	0	0	0	0.26

$$V_{tk} := \text{DATA}_{17,5} \cdot \text{gal}$$

$$V_{tk} = 5.493 \times 10^3 \text{ gal}$$

$$V_{sL} := \text{DATA}_{15,5} \cdot \text{gal}$$

$$M_{tk} := \text{DATA}_{16,5} \cdot \text{kg}$$

$$M_{tk} = 5.399 \times 10^3 \text{ lb}$$

$$V_{sL} = 2.37 \times 10^3 \text{ L}$$

$$V_L := \text{DATA}_{14,5} \cdot \text{gal}$$

$$V_L = 4.867 \times 10^3 \text{ gal}$$

$$V_{\text{gas}} := \text{DATA}_{19,5} \cdot \text{gal}$$

$$V_{\text{gas}} = 3.043 \times 10^3 \text{ gal}$$

Molecular Weights

$$MW_{\text{air}} := 29 \frac{\text{gm}}{\text{mol}}$$

$$MW_{\text{O}_2} := 32 \frac{\text{gm}}{\text{mol}}$$

$$MW_{\text{H}_2\text{O}} := 18 \frac{\text{gm}}{\text{mol}}$$

$$MW_{\text{Cl}} := 35.5 \frac{\text{gm}}{\text{mol}}$$

$$MW_{\text{TCE}} := 131.5 \frac{\text{gm}}{\text{mol}}$$

$$MW_{\text{TCA}} := 133.5 \frac{\text{gm}}{\text{mol}}$$

$$MW_{\text{PCE}} := (4 \cdot 35.5 + 2 \cdot 12) \frac{\text{gm}}{\text{mol}}$$

$$MW_{\text{PCE}} = 166 \frac{\text{gm}}{\text{mol}}$$

$$MW_{\text{PCB}} := 327 \frac{\text{gm}}{\text{mol}}$$

$$MW_{\text{HgCl}_2} := (200 + 71) \frac{\text{gm}}{\text{mol}}$$

$$MW_{\text{HgCl}_2} = 271 \frac{\text{gm}}{\text{mol}}$$

Densities

$$\rho_{\text{H}_2\text{O}} := 1 \frac{\text{kg}}{\text{L}}$$

$$\rho_L := 1 \frac{\text{kg}}{\text{L}}$$

$$\rho_s := \text{DATA}_{18,5} \cdot \frac{\text{kg}}{\text{L}}$$

$$\rho_g := \frac{P \cdot MW_{\text{air}}}{R_g \cdot T_g}$$

$$\rho_g = 1.01 \frac{\text{kg}}{\text{m}^3}$$

Tank and mixer data

Impeller diameter

Agitator speed

$$D_{\text{imp}} := 49 \text{ in}$$

$$N_{\text{act}} := 68 \frac{2 \cdot \pi}{\text{min}}$$

$$D_{tk} := 10 \text{ ft}$$

$$A_{tk} := \frac{\pi}{4} \cdot D_{tk}^2$$

$$P_{ow_act} := 3.5\text{hp} \quad (\text{Ashworth 2004b})$$

Forces

$$\text{Surface tension} \quad g_{\text{sub c}} (g_c)$$

$$\sigma := 73 \frac{\text{dyne}}{\text{cm}} \quad g_c := 32.2 \frac{\text{lb} \cdot \text{ft}}{\text{lbf} \cdot \text{s}^2}$$

Transport and Thermodynamics

$$\mu_L := 0.65 \cdot 10^{-3} \frac{\text{lb}}{\text{ft} \cdot \text{s}} \quad \mu_g := 1.2 \cdot 10^{-5} \frac{\text{lb}}{\text{ft} \cdot \text{s}} \quad \mu_g = 1.786 \times 10^{-5} \frac{\text{kg}}{\text{m} \cdot \text{s}}$$

Use Graham's Law to find diffusivities of dissolved gases in liquids D_{Aw} knowing oxygen (Thibodeaux 1979):

$$D_{O2w} := 2.5 \cdot 10^{-5} \frac{\text{cm}^2}{\text{s}} \quad D_{O2w} = 2.5 \times 10^{-9} \frac{\text{m}^2}{\text{s}}$$

$$D_{PCEw} := \sqrt{\frac{MW_{O2}}{MW_{PCE}}} \cdot D_{O2w} \quad D_{PCEw} = 1.098 \times 10^{-9} \frac{\text{m}^2}{\text{s}}$$

$$D_{TCAw} := \sqrt{\frac{MW_{O2}}{MW_{TCE}}} \cdot D_{O2w} \quad D_{TCAw} = 1.233 \times 10^{-9} \frac{\text{m}^2}{\text{s}}$$

$$D_{TCEw} := \sqrt{\frac{MW_{O2}}{MW_{TCE}}} \cdot D_{O2w} \quad D_{TCEw} = 1.233 \times 10^{-9} \frac{\text{m}^2}{\text{s}}$$

$$D_{HgCl2w} := \sqrt{\frac{MW_{O2}}{MW_{HgCl2}}} \cdot D_{O2w} \quad D_{HgCl2w} = 8.591 \times 10^{-10} \frac{\text{m}^2}{\text{s}}$$

$$D_{PCBw} := \sqrt{\frac{MW_{O2}}{MW_{PCB}}} \cdot D_{O2w} \quad D_{PCBw} = 7.821 \times 10^{-10} \frac{\text{m}^2}{\text{s}}$$

Henry's Constants

$$H_{\text{PCE}} := 16.95 \frac{\text{L} \cdot \text{atm}}{\text{mol}}$$

$$H_{\text{TCE}} := 10 \frac{\text{L} \cdot \text{atm}}{\text{mol}}$$

$$H_{\text{TCA}} := 16.95 \frac{\text{L} \cdot \text{atm}}{\text{mol}}$$

$$H_{\text{PCB}} := 0.256 \frac{\text{L} \cdot \text{atm}}{\text{mol}}$$

The Henry's constant for HgCl_2 is not known for certain. It is estimated by previous work (Ashworth 2000) as 0.14 dimensionless and is expected conservative.

$$H_{\text{HgCl}_2} := 0.014 R_g \cdot T_g$$

$$H_{\text{HgCl}_2} = 0.342 \frac{\text{L} \cdot \text{atm}}{\text{mol}}$$

There is also a correction factor for speciation, i.e., available HgCl_2 :

$$R_{\text{Cl}_\text{Hg}} := \text{DATA}_{13,5}$$

$$R_{\text{Cl}_\text{Hg}} = 0.9$$

At this ratio, a conservative estimate is 0.2 from the speciation figure in the report body:

$$f_{\text{spec}} := \frac{0.2}{0.75}$$

$$H_{\text{HgCl}_2} := H_{\text{HgCl}_2} f_{\text{spec}}$$

$$H_{\text{HgCl}_2} = 0.091 \frac{\text{L} \cdot \text{atm}}{\text{mol}}$$

Solid-Liquid Distribution

This will be an update from previous design that provides k_D 's to each VOC that are believed to be better. There is no known k_D for HgCl_2 but it is expected to be high based on sludge and liquid data and is assigned 1000.

$$k_{\text{DHgCl}_2} := 1000 \frac{\text{L}}{\text{kg}}$$

A conservative estimate, data suggests 10,000

The k_D 's for the VOCs are from EPA/540/R-96/128 Attachment C (EPA 1996):

First, the k_{OC} 's from the same document using average values for soil (note, not a lot of variance):

Using the same f_{oc} as the previous EDF at 95% UCL

$$f_{oc} := 1.07 \cdot 10^5 \frac{\text{mg}}{\text{kg}}$$

$$k_{ocPCE} := 272 \frac{\text{L}}{\text{kg}}$$

$$k_{DPCE} := k_{ocPCE} \cdot f_{oc}$$

$$k_{DPCE} = 29.104 \frac{\text{L}}{\text{kg}}$$

$$k_{ocTCA} := 139 \frac{\text{L}}{\text{kg}}$$

$$k_{DTCA} := k_{ocTCA} \cdot f_{oc}$$

$$k_{DTCA} = 14.873 \frac{\text{L}}{\text{kg}}$$

$$k_{ocTCE} := 97 \frac{\text{L}}{\text{kg}}$$

$$k_{DTCE} := k_{ocTCE} \cdot f_{oc}$$

$$k_{DTCE} = 10.379 \frac{\text{L}}{\text{kg}}$$

Note: these are lower than previously used

For PCB (using Aroclor 1260)

Note, determining PCB for other usage in project

$$K_{ow_Aroclor1260} := 10^{6.5} \frac{\text{L}}{\text{kg}}$$

(From Hemond et al. 1993)

$$K_{ocPCB} := 10^{1.00 \cdot \log \left(\frac{K_{ow_Aroclor1260}}{\text{UnitsOf}(K_{ow_Aroclor1260})} \right) - 0.21} \frac{\text{L}}{\text{kg}}$$

$$K_{ocPCB} = 1.95 \times 10^3 \frac{\text{L}}{\text{kg}}$$

$$k_{DPCB} := K_{ocPCB} \cdot f_{oc}$$

$$k_{DPCB} = 208.633 \frac{\text{L}}{\text{kg}}$$

Mass Transfer Correlations for sparge ring-agitator systems

$$b := 0.002 \text{ W}^{-0.7} \cdot \text{m}^{1.9} \cdot \text{s}^{-0.8}$$

(Perry et al. 1984)

The liquid phase mass transfer coefficient is for non-pure waters (Perry et al. 1984):

$$k_{La} = b \cdot \left(\frac{P_g}{V_{tk}} \right)^{0.7} \cdot v_g^{0.2}$$

For ionic solutions/air

$$Q_s := 1.5 \frac{\text{ft}^3}{\text{min}}$$

(Sparge nominal, will be a variable up to 40 cfm. There will be different values for different usages and the final EXCEL plots will be different.)

$$v_g := \frac{Q_s}{A_{tk}} \quad v_g = 9.7 \times 10^{-5} \frac{m}{s}$$

The P_g is the power reduced as a result of the air around the impeller. It is a function of the impeller diameter and the speed (Treybal 1987).

$$\text{Let } \Xi := \frac{Q_s}{N_{act} \cdot D_{imp}^3} \quad \Xi = 5.157 \times 10^{-5} \quad (\text{gassed power decision parameter})$$

Conditional Statement for P_g

$$P_g := \begin{cases} P_{ow_act} \cdot (0.62 - 1.85\Xi) & \text{if } \Xi > 0.037 \\ P_{ow_act} \cdot (1 - 12.2\Xi) & \text{otherwise} \end{cases} \quad \text{Note, the } P_g \text{ is the "gassed" power}$$

$$P_g = 3.5 \text{ hp} \quad P_g = 2.608 \times 10^3 \text{ W} \quad V_{tk} = 2.079 \times 10^4 \text{ L}$$

$$k_{La} := b \cdot \left(\frac{P_g}{V_{tk}} \right)^{0.7} \cdot v_g^{0.2} \quad k_{La} = 9.275 \times 10^{-3} \text{ s}^{-1}$$

Since this is for air, adjust for TCE related to the diffusivities in water for the two solutes by (Thibodeaux 1979, Crowl et al. 1990):

$$\frac{k_{La_i}}{k_{La_air}} = \left(\frac{D_i}{D_{air}} \right)^{\frac{2}{3}} \quad k_{LaPCB} := k_{La} \cdot \left(\frac{MW_{air}}{MW_{PCB}} \right)^{\frac{1}{3}}$$

$$k_{LaPCE} := k_{La} \cdot \left(\frac{MW_{air}}{MW_{PCE}} \right)^{\frac{1}{3}} \quad k_{LaTCA} := k_{La} \cdot \left(\frac{MW_{air}}{MW_{TCA}} \right)^{\frac{1}{3}}$$

$$k_{LaHgCl2} := k_{La} \cdot \left(\frac{MW_{air}}{MW_{HgCl2}} \right)^{\frac{1}{3}} \quad k_{LaTCE} := k_{La} \cdot \left(\frac{MW_{air}}{MW_{TCE}} \right)^{\frac{1}{3}}$$

II. Models for scope of effort

slow, limited sparging w/o any recirculation
add mixer operation
and then add recirculation

Slow, limited sparging w/o any recirculation

The Sherwood number, as usual, is a function of the Re and Sc. It is assumed that the liquid concentration stays constant, replenished by the sludge for the short time period.

$$Sh = 2 + b \cdot Re_G^{0.779} \cdot Sc_L^{0.546} \cdot \left(\frac{d_p \cdot g^{0.333}}{D_L^{0.667}} \right)$$

The gas Re is calculated with the slip velocity and for the single bubble regime, the slip velocity is the bubble terminal velocity. The bubble size depends on the flow regime. The sparge ring has 1/8-in. hole spaced 5/8-in. apart:

hole spacing	ring diameter	ring circumference	hole diameter	
$x_s := \frac{5}{8} \text{ in}$	$D_s := 44 \text{ in}$	$L_s := \pi \cdot D_s$	$D_o := \frac{1}{8} \text{ in}$	$L_s = 3.511 \text{ m}$

number of holes

$n_o := \frac{L_s}{x_s}$	$n_o = 221.168$	$\omega_s := \frac{Q_s}{R_{star}}$	$\omega_s = 0.032 \text{ katal}$
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The following sparge flow will vary so that the VOCs < 2 lb/hr

$Q_o := \frac{Q_s}{n_o}$	$\Delta\rho := \rho_L - \rho_g$	
$v_o := \frac{4 \cdot Q_o}{\pi \cdot D_o^2}$	$Re_o := \frac{D_o \cdot v_o \cdot \rho_g}{\mu_g}$	$Re_o = 72.463$

To determine the flow regime (Treybal 1987), a factor is used to compare Q_o with, call it Ω .

$$\Omega_b := \left[20 \cdot \frac{(\sigma \cdot D_o \cdot g_c)^5}{(g \cdot \Delta \rho)^2 \cdot \rho_L^3} \right]^{\frac{1}{6}} \quad \Omega_b = 2.279 \times 10^{-6} \frac{m^3}{s}$$

$$\frac{Q_o}{\Omega_b} = 1.405 \quad \text{Since this ratio} > 1 \text{ and } Re_o < 2100, \text{ the flow regime is intermediate}$$

$$d_p := 0.0287 m^{0.5} \cdot \sqrt{D_o} \cdot \sqrt[3]{Re_o} \quad d_p = 6.742 mm$$

$$v_t := \sqrt{\frac{2 \cdot \sigma \cdot g_c}{d_p \cdot \rho_L} + \frac{g \cdot d_p}{2}} \quad v_t = 0.234 \frac{m}{s} \quad \text{This is the bubble terminal velocity}$$

$$\beta := 0.845 \quad \alpha := 1.36 \quad \gamma := -1.39 \times 10^{-5} \quad v_s \text{ versus } v_g \text{ correlation determined from Treybal 1987, Figure 6.2. (Ashworth 2004a)}$$

$$v_s := \frac{v_g}{\alpha \cdot \left(v_g \cdot \frac{s}{m} \right)^\beta + \gamma} \quad v_s = 0.179 \frac{m}{s} \quad \text{Note: there shouldn't be a lot of difference between } v_s \text{ and } v_t.$$

The gas Re is then (note that this Re uses the slip velocity):

$$Re_G := \frac{d_p \cdot v_s \cdot \rho_L}{\mu_L} \quad Re_G = 1.251 \times 10^3$$

The Schmidt number is different for each VOC, for the liquid (using PCE) is:

$$Sc_{PCE} := \frac{\mu_L}{\rho_L \cdot D_{PCEw}} \quad b_{Sh} := 0.018 \quad \text{For swarms of bubbles}$$

$$Sh_{PCE} := 2 + b_{Sh} \cdot Re_G^{0.779} \cdot Sc_{PCE}^{0.546} \cdot \left(\frac{\frac{1}{d_p \cdot g^{\frac{3}{2}}}}{\frac{2}{D_{PCEw}^3}} \right)^{0.116} \quad Sh_{PCE} = 593.442$$

$$k_{LPCE} := \frac{Sh_{PCE} D_{PCEw}}{d_p} \quad k_{LPCE} = 9.662 \times 10^{-5} \frac{m}{s}$$

Need a holdup to determine the bubble specific surface area, since there is no real liquid velocity:

$$\phi := \frac{v_g}{v_s} \quad \phi = 5.407 \times 10^{-4}$$

$$a := \frac{6 \cdot \phi}{d_p} \quad a = 0.481 \frac{m^2}{m^3}$$

$$k_{La_PCE} := k_{LPCE} a \quad k_{La_PCE} = 4.649 \times 10^{-5} \frac{1}{s}$$

$$C_{PCE} := DATA_{1,4} \cdot \frac{mg}{L} \quad C_{PCE} = 0.35 \frac{mg}{L}$$

This next section for liquids includes two more methods for comparison, a different Sh method and using penetration theory.

Different Sh Method (Bennett and Myers 1962)

This uses a different Re based on bubble. The velocity u_o is the relative velocity between the liquid and the gas, i.e., v_s .

$$u_o := v_s \quad Re_p := \frac{d_p \cdot u_o \cdot \rho_L}{\mu_L} \quad Re_p = 1.251 \times 10^3$$

$$Sh_{PCE} := 2 + 0.6 Sc_{PCE}^{\frac{1}{3}} \cdot Re_p^{\frac{1}{2}} \quad Sh_{PCE} = 205.44$$

$$k_{LPCE} := \frac{Sh_{PCE} D_{PCEw}}{d_p} \quad k_{LPCE} = 3.345 \times 10^{-5} \frac{m}{s}$$

This is smaller. However, it is not an exact analog as the above is more akin to heat transfer analogies of a fluid flowing past spheres. In any case, the previous value is more conservative.

Higbie Penetration Theory (Bird et al. 1960)

The contact time is the distance/terminal velocity:

$$z := 10\text{ft}$$

$$\theta := \frac{z}{v_t}$$

$$k_{LPCE} := 2 \cdot \sqrt{\frac{D_{PCEw}}{\pi \cdot \theta}}$$

$$k_{LPCE} = 1.036 \times 10^{-5} \frac{\text{m}}{\text{s}}$$

The distance for contact is difficult to assign. Again, the previous k_L is conservative.

Transients/ $C(t)$, $X(t)$, and $Y(t)$

For the transients and the pressure relations when sparging (Note: a relation called the stripping factor that is a non-equilibrium gas factor that applies at fairly low sparge rates).

At any time, t:

$$\omega(t) = k_{La} \left(C_i(t) - \frac{p_i(t)}{H_i} \right) \cdot V$$

$$\frac{p_i}{P} = \frac{\omega(t)}{\omega(t) + \omega_s}$$

$$\text{if } \omega(t) < \omega_s \quad \frac{p_i}{P} = \frac{\omega(t)}{\omega_s}$$

$$\omega(t) = \omega_s \cdot \frac{p_i}{P}$$

$$\omega_s \cdot \frac{p_i}{P} = k_{La} \left(C_i(t) - \frac{p_i(t)}{H_i} \right) \cdot V$$

$$p_i \left(\frac{\omega_s}{P} + \frac{k_{La} \cdot V}{H_i} \right) = k_{La} \cdot C_i \cdot V$$

$$p_i = \frac{k_{La} \cdot V}{\frac{\omega_s}{P} + \frac{k_{La} \cdot V}{H_i}} \cdot C_i$$

$$p_i = \lambda_i \cdot C_i$$

$$\lambda_i = \frac{k_{Li} \cdot a \cdot V}{\frac{\omega_s}{P} + \frac{k_{Li} \cdot a \cdot V}{H_i}}$$

$$\frac{d}{dt} C_i = k_{Li} \cdot a \cdot \left(C_i - \frac{p_i}{H_i} \right)$$

$$\frac{d}{dt}C_i = -k_{Li} \cdot a \cdot C_i \left(1 - \frac{\lambda_i}{H_i}\right) \quad C_i(t) = C_{i0} \cdot e^{-k_{Li} \cdot a \cdot \left(1 - \frac{\lambda_i}{H_i}\right) \cdot t}$$

Example at 1.5 cfm with C_{PCE} the initial concentration out of the data matrix (these relations, e.g., $C_i(t)$ and λ are used in the model by input into EXCEL):

$$\lambda_{PCE} := \frac{k_{LaPCE} V_L}{\frac{\omega_s}{P} + \frac{k_{LaPCE} V_L}{H_{PCE}}} \quad \lambda_{PCE} = 16.839 \frac{L \cdot atm}{mol}$$

$$p_{PCE} := \frac{C_{PCE}}{MW_{PCE}} \cdot \lambda_{PCE} \quad p_{PCE} = 3.55 \times 10^{-5} atm$$

$$\omega_{PCE} := k_{LaPCE} V_L \cdot \left(\frac{C_{PCE}}{MW_{PCE}} - \frac{p_{PCE}}{H_{PCE}} \right) \quad \omega_{PCE} = 1.319 \times 10^{-6} \frac{mol}{s}$$

Note how this differs from when using the solid in the driving force (below). Also, at high sparge rate, $\lambda \rightarrow 0$, a standard assumption for many calculations and that when $\omega_s \rightarrow 0$, the gas is at equilibrium with the liquid and there is no mass transfer (this can be seen by doing this in the λ equation and noting that $k_L a$ increases with flow to a power less than one).

Add Mixer operation

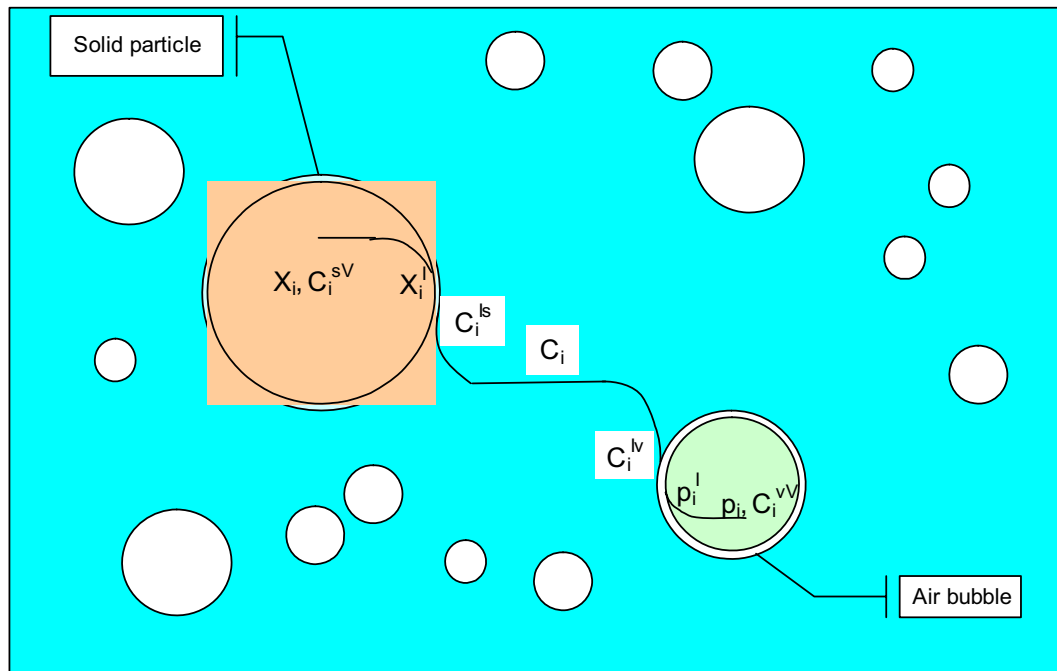
At the point juncture of turning on the mixer, the concentrations start declining and the gas phase increases. Note that the equilibrium concentration will exceed these prior to start of air. This is the same model as before (Ashworth 2004a) but is derived below.

The figure below shows mass transfer from a solid sludge particle to a liquid (mainly water) followed by the liquid to air bubbles. There are five liquid concentrations, two solid concentrations, and two vapor concentrations. These are defined below:

X_i	Bulk solid concentration, mg/kg
X_i^I	Interface solid concentration, mg/kg
C_i^{sV}	Nonexistent (virtual) liquid concentration in solid, mg/L
C_i^{Is}	Interface liquid concentration at solid, mg/L
C_i	Bulk liquid concentration, mg/L
C_i^{Iv}	Interface liquid concentration at bubble, mg/L
C_i^{vV}	Nonexistent (virtual) liquid concentration in bubble, mg/L
p_i^I	Interface partial pressure, atm
p_i	Bulk partial pressure, atm

Equilibrium holds at the interfaces:

$$X_i^I = k_D \cdot C_i^{Is} \quad p_i^I = H \cdot C_i^{Iv}$$



Transfer relations (note heat transfer analogies):

$$N_i = k_S \cdot (X_i - X_i^I) = k_L \cdot (C_i^{Is} - C_i^{Iv}) = k_G \cdot (p_i^I - p_i) \quad (\text{See Thibodeaux 1979 for similar})$$

$$\frac{N_i}{K_L^{oa}} = (C_i^{sV} - C_i^{Is}) + (C_i^{Is} - C_i^{Iv}) + (C_i^{Iv} - C_i^{vV})$$

$$\frac{N_i}{K_L^{oa}} = \frac{1}{k_D} \cdot (X_i - X_i^I) + \frac{N_i}{k_L} + \frac{1}{H} \cdot (p_i^I - p_i)$$

$$\frac{1}{K_L^{oa}} = \frac{1}{k_D \cdot k_S} + \frac{1}{k_L} + \frac{1}{H \cdot k_G} \quad \text{or} \quad K_L^{oa} = \frac{1}{\frac{1}{k_D \cdot k_S} + \frac{1}{k_L} + \frac{1}{H \cdot k_G}}$$

For the heat transfer analogy that helps clarify the math in this, use heat transfer through a composite wall:

$$q = h_o \cdot (T_o - T_{w1o}) = \frac{k_1}{x_1} \cdot (T_{w1o} - T_{w1i}) = \frac{k_2}{x_2} \cdot (T_{w1i} - T_{w2o}) = h_i \cdot (T_{w2o} - T_i)$$

$$U_{oa} = \frac{1}{\frac{1}{h_o} + \frac{x_1}{k_1} + \frac{x_2}{k_2} + \frac{1}{h_i}}$$

The overall heat transfer coefficient is the reciprocal of the sum of the individual resistances.

To avoid virtual liquid concentrations in the useable transfer functions, would like the coefficient based on the solid. This is done by using all solid concentration driving forces:

$$\frac{N_i}{K_S^{oa}} = (X_i - X_i^I) + k_D \cdot (C_i^{Is} - C_i^{Iv}) + \frac{k_D}{H} \cdot (p_i^I - p_i)$$

$$\frac{1}{K_S^{oa}} = \frac{1}{k_S} + \frac{k_D}{k_L} + \frac{k_D}{H \cdot k_G} \quad K_S^{oa} = \frac{1}{\frac{1}{k_S} + \frac{k_D}{k_L} + \frac{k_D}{H \cdot k_G}}$$

In these types of mass transfer, k_G is normally assumed large enough to be ignored. The overall coefficient is therefore a combination of solid and liquid coefficients. The mean solid size is 144 μm and it is assumed the void fraction is 0.5.

$$K_S^{oa} = \frac{1}{\frac{1}{k_S} + \frac{k_D}{k_L}} \quad Sh = 2 + 0.72 Re_p^{\frac{1}{2}} \cdot Sc^{\frac{1}{3}} \quad \text{For solids being mixed with liquids}$$

$$Sh = \frac{k_S \cdot a_s \cdot d_p^2}{D_{iw}} \quad (\text{Oldshue 1983, Harnby 1992}) \quad \lim_{d_p \rightarrow 0} Sh = 2$$

$$k_S = \frac{2 \cdot D_{iw}}{a_s \cdot d_s^2} \quad k_S \cdot a = \frac{2 \cdot D_{iw}}{d_s^2}$$

$$K_{Sa} = \frac{1}{\left(\frac{1}{k_S \cdot a \cdot \rho_s} + \frac{k_D}{k_{La}} \right) \cdot \rho_s}$$

For the mass transfer from the solid to the gas across 2 interfaces:

$$\omega(t) = K_{Sa} \cdot \left(X_i - \frac{k_D \cdot p_i(t)}{H_i} \right) \cdot M$$

Need to estimate the back partial pressure, p_i to remove as a variable.

$$\frac{p_i}{P} = \frac{\omega(t)}{\omega(t) + \omega_s}$$

$$\text{if } \omega(t) < \omega_s \quad \frac{p_i}{P} = \frac{\omega(t)}{\omega_s} \quad \omega(t) = \omega_s \cdot \frac{p_i}{P}$$

$$\omega_s \cdot \frac{p_i}{P} = K_{Sa} \cdot \left(X_i - \frac{k_D \cdot p_i}{H_i} \right) \cdot M$$

$$p_i \cdot \left(\frac{\omega_s}{P} + \frac{K_{Sa} \cdot M \cdot k_D}{H_i} \right) = K_{Sa} \cdot X_i \cdot M$$

$$p_i = \frac{K_{Sa} \cdot X_i \cdot M}{\frac{\omega_s}{P} + \frac{K_{Sa} \cdot M \cdot k_D}{H_i}} = \Lambda_i \cdot X_i$$

$$\Lambda_i = \frac{K_{Sa} \cdot M}{\frac{\omega_s}{P} + \frac{K_{Sa} \cdot M \cdot k_D}{H_i}}$$

$$\frac{d}{dt} X_i = -K_{Sa} \cdot \left(X_i - \frac{k_{Di} \cdot \Lambda_i}{H_i} \right)$$

$$\frac{d}{dt} X_i = -K_{Sa} \cdot X_i \cdot \left(1 - \frac{\Lambda_i \cdot k_{Di}}{H_i} \right)$$

$$X_i(t) = X_{i0} \cdot e^{-K_{Sa} \cdot \left(1 - \frac{\Lambda_i \cdot k_{Di}}{H_i} \right) \cdot t}$$

Mean particle diameter

$$d_s := 144 \mu\text{m}$$

The mass rate of Hg and PCB is desired for the flowsheet and at 40 cfm for regulatory purposes:

$$k_{SaHg} := \frac{2 \cdot D_{HgCl2w}}{d_s^2}$$

$$k_{SaHg} = 0.083 \frac{1}{s}$$

$$K_{SaHg} := \frac{1}{\left(\frac{1}{k_{SaHg} \cdot \rho_s} + \frac{k_{DHgCl2}}{k_{LaHgCl2}} \right) \cdot \rho_s}$$

$$K_{SaHg} = 4.275 \times 10^{-6} \frac{1}{s}$$

$$\Lambda_{HgCl2} := \frac{K_{SaHg} \cdot M_{tk}}{\frac{\omega_s}{P} + \frac{K_{SaHg} \cdot M_{tk} \cdot k_{DHgCl2}}{H_{HgCl2}}}$$

$$\Lambda_{HgCl2} = 0.00009 \frac{\text{kg} \cdot \text{atm}}{\text{mol}}$$

$$X_{Hg} := \text{DATA}_{11,5} \frac{\text{mg}}{\text{kg}}$$

$$x_{HgCl2} := X_{Hg} \cdot \frac{1}{MW_{HgCl2}}$$

$$x_{HgCl2} = 3.218 \times 10^{-3} \frac{\text{mol}}{\text{kg}}$$

Saturation k_D (see Valsaraj 1995)

$$k_{Dsat} := \frac{k_{DHgCl2} R_g \cdot T_g}{H_{HgCl2}}$$

$$k_{Dsat} = 2.679 \times 10^5 \frac{\text{L}}{\text{kg}}$$

$$p_{\text{HgCl}_2} := \Lambda_{\text{HgCl}_2} x_{\text{HgCl}_2}$$

$$p_{\text{HgCl}_2} = 2.936 \times 10^{-7} \text{ atm}$$

In terms of mg/m^3

$$y_{\text{HgCl}_2} := \frac{p_{\text{HgCl}_2}}{R_g \cdot T_g} \cdot \text{MW}_{\text{HgCl}_2}$$

$$y_{\text{HgCl}_2} = 3.254 \frac{\text{mg}}{\text{m}^3}$$

$$\Lambda_{\text{HgCl}_2} := \frac{K_{\text{SaHg}} \cdot M_{\text{tk}}}{40 \frac{\text{ft}^3}{\text{min}} R_{\text{star}} + \frac{K_{\text{SaHg}} \cdot M_{\text{tk}} \cdot k_{\text{DHgCl}_2}}{H_{\text{HgCl}_2}}}$$

$$p_{\text{HgCl}_2} := \Lambda_{\text{HgCl}_2} x_{\text{HgCl}_2}$$

$$p_{\text{HgCl}_2} = 2.912 \times 10^{-7} \text{ atm}$$

$$y_{\text{HgCl}_2} := \frac{p_{\text{HgCl}_2}}{R_g \cdot T_g} \cdot \text{MW}_{\text{HgCl}_2}$$

$$y_{\text{HgCl}_2} = 3.228 \frac{\text{mg}}{\text{m}^3}$$

$$w_{\text{Hg}} := k_{\text{LaHgCl}_2} \left(\frac{x_{\text{HgCl}_2}}{k_{\text{DHgCl}_2}} - \frac{p_{\text{HgCl}_2}}{H_{\text{HgCl}_2}} \right) \cdot V_{\text{sL}} \cdot \text{MW}_{\text{HgCl}_2}$$

$$w_{\text{Hg}} = 6.186 \times 10^{-4} \frac{\text{lb}}{\text{hr}}$$

Then, dilute by the stack flow of 400 scfm:

$$y_{\text{Hgstk}} := y_{\text{HgCl}_2} \frac{40}{400}$$

$$y_{\text{Hgstk}} = 0.323 \frac{\text{mg}}{\text{m}^3}$$

For PCBs

$$k_{\text{SaPCB}} := \frac{2 \cdot D_{\text{PCBw}}}{d_s^2}$$

$$k_{\text{SaPCB}} = 0.075 \frac{1}{\text{s}}$$

$$K_{\text{SaPCB}} := \frac{1}{\left(\frac{1}{k_{\text{SaPCB}} \cdot \rho_s} + \frac{k_{\text{DPCB}}}{k_{\text{SaPCB}}} \right) \cdot \rho_s}$$

$$K_{\text{SaPCB}} = 3.494 \times 10^{-4} \frac{1}{\text{s}}$$

$$\Lambda_{\text{PCB}} := \frac{K_{\text{SaPCB}} \cdot M_{\text{tk}}}{\frac{\omega_s}{P} + \frac{K_{\text{SaPCB}} \cdot M_{\text{tk}} \cdot k_{\text{DPCB}}}{H_{\text{PCB}}}}$$

$$\Lambda_{\text{PCB}} = 0.00123 \frac{\text{kg} \cdot \text{atm}}{\text{mol}}$$

$$X_{\text{PCB}} := \text{DATA}_{10,5} \frac{\text{mg}}{\text{kg}}$$

$$x_{\text{PCB}} := X_{\text{PCB}} \frac{1}{\text{MW}_{\text{PCB}}}$$

$$x_{\text{PCB}} = 4.954 \times 10^{-4} \frac{\text{mol}}{\text{kg}}$$

$$p_{\text{PCB}} := \Lambda_{\text{PCB}} \cdot x_{\text{PCB}}$$

$$p_{\text{PCB}} = 6.079 \times 10^{-7} \text{ atm}$$

In terms of ppm_v

$$Y_{\text{PCB}} := \frac{p_{\text{PCB}}}{P}$$

$$Y_{\text{PCB}} = 0.715 \text{ ppm}_v$$

$$\Lambda_{\text{PCB}} := \frac{K_{\text{SaPCB}} \cdot M_{\text{tk}}}{\frac{40 \frac{\text{ft}^3}{\text{min}} \cdot R_{\text{star}}}{P} + \frac{K_{\text{SaPCB}} \cdot M_{\text{tk}} \cdot k_{\text{DPCB}}}{H_{\text{PCB}}}}$$

$$p_{\text{PCB}} := \Lambda_{\text{PCB}} \cdot x_{\text{PCB}}$$

$$p_{\text{PCB}} = 6.07 \times 10^{-7} \text{ atm}$$

$$w_{\text{PCB}} := K_{\text{SaPCB}} \left(\frac{X_{\text{PCB}}}{\text{MW}_{\text{PCB}}} - \frac{k_{\text{DPCB}} p_{\text{PCB}}}{H_{\text{PCB}}} \right) \cdot M_{\text{tk}} \cdot \text{MW}_{\text{PCE}}$$

$$w_{\text{PCB}} = 1.561 \times 10^{-3} \frac{\text{lb}}{\text{hr}}$$

$$Y_{\text{PCB}} := \frac{p_{\text{PCB}}}{P}$$

$$Y_{\text{PCB}} = 0.714 \text{ ppm}_v$$

Then, dilute by the stack flow of 400 scfm:

$$Y_{\text{PCBstk}} := Y_{\text{PCB}} \frac{40}{400}$$

$$Y_{\text{PCBstk}} = 0.071 \text{ ppm}_v$$

The others are done in a similar fashion and put into EXCEL for multiple calculations.

$$k_{\text{SaPCE}} := \frac{2 \cdot D_{\text{PCEw}}}{d_s^2} \quad k_{\text{SaPCE}} = 0.106 \frac{1}{s}$$

$$K_{\text{SaPCE}} := \frac{1}{\left(\frac{1}{k_{\text{SaPCE}} \rho_s} + \frac{k_{\text{DPCE}}}{k_{\text{LaPCE}}} \right) \cdot \rho_s} \quad K_{\text{SaPCE}} = 1.727 \times 10^{-4} \frac{1}{s}$$

$$\Lambda_{\text{PCE}} := \frac{K_{\text{SaPCE}} M_{\text{tk}}}{\frac{\omega_s}{P} + \frac{K_{\text{SaPCE}} M_{\text{tk}} \cdot k_{\text{DPCE}}}{H_{\text{PCE}}}} \quad \Lambda_{\text{PCE}} = 0.55404 \frac{\text{kg} \cdot \text{atm}}{\text{mol}}$$

$$X_{\text{PCE}} := \text{DATA}_{7,5} \frac{\text{mg}}{\text{kg}} \quad x_{\text{PCE}} := X_{\text{PCE}} \frac{1}{\text{MW}_{\text{PCE}}}$$

$$x_{\text{PCE}} = 8.524 \times 10^{-3} \frac{\text{mol}}{\text{kg}} \quad X_{\text{PCE}} = 1.415 \times 10^3 \frac{\text{mg}}{\text{kg}}$$

Saturation k_D

$$k_{\text{Dsat}} := \frac{k_{\text{DPCE}} R_g \cdot T_g}{H_{\text{PCE}}} \quad k_{\text{Dsat}} = 41.983 \frac{\text{L}}{\text{kg}}$$

$$p_{\text{PCE}} := \Lambda_{\text{PCE}} x_{\text{PCE}} \quad p_{\text{PCE}} = 4.723 \times 10^{-3} \text{ atm}$$

In terms of ppm_v:

$$Y_{\text{PCE}} := \frac{p_{\text{PCE}}}{P} \quad Y_{\text{PCE}} = 5.556 \times 10^3 \text{ ppm}_v$$

Check assumption low mass transfer assumption:

$$\frac{\omega_{\text{PCE}}}{\omega_s} = 4.177 \times 10^{-5} \quad \text{Indicating a good assumption}$$

Check the mass transfer rate:

$$\omega_{PCE} := K_{SaPCE} \left(\frac{X_{PCE}}{MW_{PCE}} - \frac{k_{DPCE} P_{PCE}}{H_{PCE}} \right) \cdot M_{tk} \quad \omega_{PCE} = 1.755 \times 10^{-4} \text{ katal}$$

$$w_{PCE} := \omega_{PCE} MW_{PCE} \quad w_{PCE} = 0.231 \frac{\text{lb}}{\text{hr}}$$

Check via initial slope:

$$r_{mi} := -K_{SaPCE} X_{PCE} \left(1 - \frac{\Lambda_{PCE} k_{DPCE}}{H_{PCE}} \right) \cdot M_{tk} \quad r_{mi} = -0.231 \frac{\text{lb}}{\text{hr}}$$

check via gas concentration

$$w_{PCE} := \frac{Q_s \cdot Y_{PCE} 60 \cdot \frac{\text{min}}{\text{hr}} \cdot MW_{PCE}}{R_{star}} \quad w_{PCE} = 0.231 \frac{\text{lb}}{\text{hr}} \quad \text{OK}$$

Determine equilibrium values using 3-phase box model (note: these will not match actual values provided in characterization):

The total mass of i is:

$$M_i = X_i \cdot M + C_i \cdot V_L + y_i \cdot V_{gas}$$

Relations

$$X_i = k_{Di} \cdot C_i \quad p_i = H \cdot C_i$$

Solving the three above for X_i :

$$X_i = \frac{M_i}{M + \frac{V_L}{k_{Di}} + \frac{V_{gas} \cdot R_g \cdot T_g}{k_{Di} \cdot H_i}}$$

For Hg, the mass is:

$$M_{Hg} := \text{DATA}_{27,5} \cdot \text{kg} \quad M_{Hg} = 3.01 \text{ kg}$$

$$X_{\text{HgCl}_2} := \frac{M_{\text{Hg}}}{M_{\text{tk}} + \frac{V_L}{k_{\text{DHgCl}_2}} + \frac{V_{\text{gas}} \cdot R_g \cdot T_g}{k_{\text{DHgCl}_2} H_{\text{HgCl}_2}}} \quad X_{\text{HgCl}_2} = 542.062 \frac{\text{mg}}{\text{kg}}$$

$$C_{\text{HgCl}_2} := \frac{X_{\text{HgCl}_2}}{k_{\text{DHgCl}_2}} \quad C_{\text{HgCl}_2} = 0.542 \frac{\text{mg}}{\text{L}}$$

$$p_{\text{HgCl}_2} := \frac{C_{\text{HgCl}_2}}{\text{MW}_{\text{HgCl}_2}} \cdot H_{\text{HgCl}_2} \quad p_{\text{HgCl}_2} = 1.826 \times 10^{-7} \text{ atm}$$

$$y_{\text{HgCl}_2} := \frac{p_{\text{HgCl}_2} \text{MW}_{\text{HgCl}_2}}{P \cdot R_{\text{star}}} \quad y_{\text{HgCl}_2} = 2.597 \frac{\text{mg}}{\text{m}^3}$$

$$Y_{\text{HgCl}_2} := \frac{p_{\text{HgCl}_2}}{P} \quad Y_{\text{HgCl}_2} = 0.215 \text{ ppm}_v$$

The others are done similarly and are provided in the table below.

Equilibrium: 3-phase box model									
	M _i , kg	k _o , L/kg	H _i , L-atm/mol	MW	X _i , mg/kg	C _i , mg/L	p _i , atm	y _i , mg/L	Y _i , ppm
PCE	1.44	29.10	16.95	166	395	14	1.38E-03	1.21E+01	1629
TCA	0.94	14.87	16.95	131.5	195	13	1.69E-03	1.16E+01	1985
TCE	28.59	10.38	10	133.5	4122	397	2.98E-02	2.08E+02	35002
HgCl ₂	3.01	1000.00	0.11	271	608	0.61	2.53E-07	3.60E-03	0.30
PCB	0.56	208.63	0.256	327	72	0.34	2.70E-07	4.63E-03	0.32

Add circulation

Mass transfer model for circulation and splashing

There are two modes including downward flow of liquid against air during recirculation and creation of drops by dropping on liquid surface and splashing. Modifications of these are used in entrainment discussed below. However, this is a mass transfer model(s). In the first case there are drops with VOCs transferring to surrounding air at the sparge rate of air.

$$N_i = k_L \cdot (C - C_v) \quad \text{or} \quad \omega_i = k_{La} \cdot V \cdot (C - C_v)$$

The $k_L a$ is related to drop size and flow. This model uses the penetration theory (Thib) developed by Higbie in 1935. It is better than the simple film model and does not have the problem with unknowns in the surface renewal model.

$$N_0 = \frac{2}{k_D} \cdot \sqrt{\frac{D_{iw}}{\pi \cdot \theta}} \cdot (X_i - X_i^v)$$

Need the contact time, θ :

Do not know the flow, F , so use 100 gpm.

$$D_c := 2 \text{ in}$$

$$F_c := 100 \frac{\text{gal}}{\text{min}}$$

$$A_c := \frac{\pi}{4} \cdot D_c^2$$

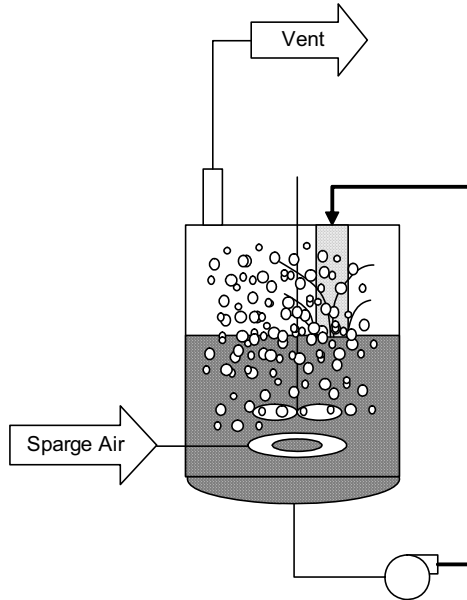
$$v_c := \frac{F_c}{A_c}$$

$$Z := 3 \text{ ft}$$

Approximate

$$\theta_1 := \frac{Z}{v_c}$$

$$\theta_1 = 0.294 \text{ s}$$



Mode 1, Circulation

It is not expected that there will be significant mass transfer for a falling column of liquid. Therefore, model as a single stage, equilibrium transfer unit.

$$F \cdot (X_o - X_i) = \omega \cdot (Y_o - Y_i)$$

F ; mass rate, gas; mole fractions, mole rates

$$Y_o = f(X_o)$$

$$X_o = \frac{\omega}{F} \cdot (Y_o - Y_i) + X_i$$

$$Y_o = \frac{p_o}{P}$$

$$p_o = X_o \cdot \frac{H_A}{k_{DA}}$$

$$X_o = \frac{\omega}{F} \cdot \left(\frac{X_o}{P} \cdot \frac{H_A}{k_{DA}} - Y_i \right) + X_i$$

$$X_o \cdot \left(1 - \frac{\omega \cdot H_A}{F \cdot k_{DA} \cdot P} \right) = X_i - \frac{\omega}{F} \cdot Y_i$$

$$X_o = \frac{X_i - \frac{\omega}{F} \cdot Y_i}{1 - \frac{\omega \cdot H_A}{F \cdot k_{DA} \cdot P}}$$

$$X_o := \frac{\frac{X_{PCE}}{MW_{PCE}} - \frac{\omega_s}{F_c \cdot \rho_L} \cdot \frac{p_{PCE}}{P}}{1 - \frac{\omega_s \cdot H_{PCE}}{F_c \cdot k_{DPCE} \cdot \rho_L \cdot P}} \cdot MW_{PCE}$$

$$X_o = 1.415 \times 10^{-3}$$

$$\frac{X_o}{X_{PCE}} = 1 \quad \text{so, it changes little and is not used}$$

Mode 2, Splashing

Using the correlations from the DOE Handbook (DOE 1994), and Ballinger (Ballinger 1993).

$$\text{Arch} := \frac{\rho_g^2 \cdot Z^3 \cdot g}{\mu_L^2}$$

$$\text{Arch} = 8.144 \times 10^6$$

The airborne release fraction (ARF) is:

$$\text{ARF} := 8.9 \cdot 10^{-10} \cdot \text{Arch}^{0.55}$$

$$\text{ARF} = 5.628 \times 10^{-6}$$

The bubble size is unknown. The DOE Handbook has $15.8 \mu\text{m} \pm 10.1$:

$$D_B := 15.8 \mu\text{m}$$

$$r_B := \frac{D_B}{2}$$

$$V_B := \frac{4}{3} \cdot \pi \cdot r_B^3$$

$$V_B = 2.065 \times 10^{-12} \text{ L}$$

So of the volume of the inlet, there are:

$$Q_B := \text{ARF} \cdot F_c$$

$$Q_B = 3.551 \times 10^{-8} \frac{\text{m}^3}{\text{s}}$$

The number of bubbles produced is:

$$n_B := \frac{Q_B}{\frac{4}{3} \cdot \pi \cdot r_B^3} \quad n_B = 1.719 \times 10^7 \frac{1}{s}$$

The individual bubble area is

$$A_B := 4 \cdot \pi \cdot r_B^2 \quad A_B = 7.843 \times 10^{-10} \text{ m}^2$$

Average bubble velocity is:

$$m \cdot v = \sum_i (m_i \cdot v_i) \quad \text{by momentum balance}$$

$$\rho_L \cdot \frac{F_c}{A_c} = n_B \cdot \theta_1 \cdot v \cdot \rho_L \quad v_B := \frac{F_c}{n_B \cdot \theta_1 \cdot A_c} + v_g \quad v_B = 9.764 \times 10^{-5} \frac{\text{m}}{\text{s}}$$

The area for mass transfer is:

$$A_s := n_B \cdot A_B \quad A_s = 0.013 \frac{\text{m}^2}{\text{s}}$$

$$a_s := \frac{A_s}{Q_B} \quad a_s = 3.797 \times 10^5 \frac{1}{\text{m}}$$

$$\theta_2 := \frac{Z}{v_B} \quad \theta_2 = 9.365 \times 10^3 \text{ s}$$

Example calculation for PCE

$$k_{LPCE} := 2 \cdot \sqrt{\frac{D_{PCEw}}{\pi \cdot \theta_2}} \quad k_{LPCE} = 3.863 \times 10^{-7} \frac{\text{m}}{\text{s}}$$

$$k_{LaPCE} := k_{LPCE} a_s \quad k_{LaPCE} = 0.147 \frac{1}{\text{s}}$$

$$k_{LaPCE} = 0.147 \frac{1}{s} \quad \text{while this is large, it doesn't operate on a large mass}$$

The initial maximum mass transfer rate is

$$w := k_{LaPCE} Q_B \cdot \rho_L \cdot \theta_2 \cdot \left(X_{PCE} - \frac{p_{PCE} k_{DPCE} MW_{PCE}}{H_{PCE}} \right)$$

$$w = 0.027 \frac{\text{lb}}{\text{hr}} \quad Q_B \cdot \rho_L \cdot \theta_2 = 0.333 \text{ kg}$$

III. Flowsheet and HVAC Balance

Using a flow of 450 scfm, and a VOC emission rate of 2 lb/hr, an approximate VOC concentration is estimated:

$$r_{VOC} := 2 \frac{\text{lb}}{\text{hr}} \quad Q_v := 450 \frac{\text{ft}^3}{\text{min}}$$

$$Y_{VOC} := \frac{r_{VOC} R_{star}}{Q_v \cdot MW_{PCE}} \quad Y_{VOC} = 160.204 \text{ ppm}_v$$

Entrainment of Radionuclides

To find the loadings for radionuclides, an entrainment function is needed. There is quite a bit of data available for entrainment of bubbling liquids from the DOE Handbook (DOE 1994) shown in the plot below. The line for small vapor velocity (0.25 cm/s) was used as it has the steepest slope and the data included it. This was also done for an earlier demister design (Ashworth 2005).

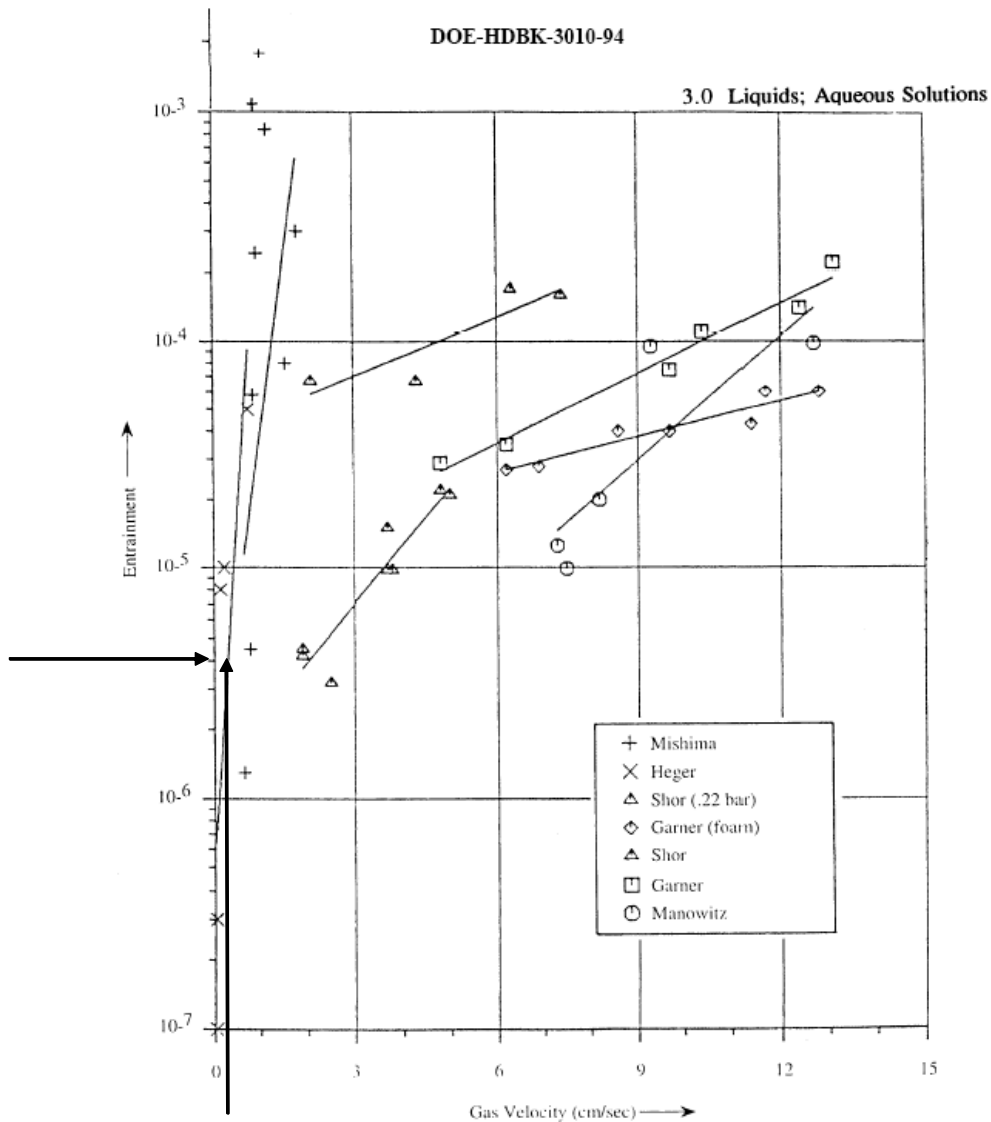


Figure 3-2. Entrainment Data Obtained at Small Gas Velocity
(Borkowski, Bunz, and Schoeck May 1986)

From their Figure 3-2 and using their definition of entrainment (i.e., vapor mass velocities, G):

Worse-case sparge, i.e., this value will not be exceeded (due to HVAC balance):

$$Q_v := 40 \frac{\text{ft}^3}{\text{min}}$$

$$v_g := \frac{4 \cdot Q_s}{\pi \cdot D_{tk}^2}$$

$$v_g = 0.259 \frac{\text{cm}}{\text{s}}$$

$$E := 4 \cdot 10^{-6}$$

From intersection of v_g with Heger data in above plot

$$G_v := v_g \cdot \rho_g$$

$$G_v = 0.032 \frac{\text{lb}}{\text{ft}^2 \cdot \text{min}}$$

$$G_{dplt} := E \cdot G_v$$

$$G_{dplt} = 1.28 \times 10^{-7} \frac{\text{lb}}{\text{ft}^2 \cdot \text{min}}$$

This is the flux or mass velocity of water drops, for the radionuclide flux, multiply by the concentration, e.g.:

Gamma emitters ^{137}Cs , ^{63}Ni , and ^{60}Co

Concentrations based on un-dissolved:

$$C_{Cs} := 7.35 \cdot 10^3 \frac{\text{nCi}}{\text{gm}}$$

$$C_{Ni} := 10^3 \frac{\text{nCi}}{\text{gm}}$$

$$C_{Co} := 397 \frac{\text{nCi}}{\text{gm}}$$

$$G_{Cs} := G_{dplt} \cdot C_{Cs}$$

$$G_{Cs} = 0.427 \frac{\text{nCi}}{\text{ft}^2 \cdot \text{min}}$$

The rate would be for ^{137}Cs :

$$r_{Cs} := G_{Cs} \cdot \frac{\pi}{4} \cdot D_{tk}^2$$

$$r_{Cs} = 33.572 \frac{\text{nCi}}{\text{min}}$$

$$G_{Ni} := G_{dplt} \cdot C_{Ni}$$

$$G_{Ni} = 0.058 \frac{\text{nCi}}{\text{ft}^2 \cdot \text{min}}$$

The rate would be for ^{63}Ni :

$$r_{Ni} := G_{Ni} \cdot \frac{\pi}{4} \cdot D_{tk}^2$$

$$r_{Ni} = 4.568 \frac{\text{nCi}}{\text{min}}$$

$$G_{Co} := G_{dplt} \cdot C_{Co}$$

$$G_{Co} = 0.023 \frac{\text{nCi}}{\text{ft}^2 \cdot \text{min}}$$

The rate would be for ^{60}Co :

$$r_{\text{Co}} := G_{\text{Co}} \cdot \frac{\pi}{4} \cdot D_{\text{tk}}^2 \quad r_{\text{Co}} = 1.813 \frac{\text{nCi}}{\text{min}}$$

In addition to this entrainment, there is splashing from recirculation. A correlation for falling liquid is used for this (DOE 1994) and is correlated by the Archimedes number (Arch). It depends on several vapor/liquid parameters including the spill height z_s .

$$z_s := 34\text{in}$$

$$\text{Arch} := \frac{\rho_g \cdot z_s^3 \cdot g}{\mu_L^2} \quad \text{Arch} = 6.861 \times 10^6 \quad Q_r := 100 \frac{\text{gal}}{\text{min}}$$

The airborne release fraction (ARF) is:

$$\text{ARF} := 8.9 \cdot 10^{-10} \cdot \text{Arch}^{0.55} \quad \text{Based on DOE handbook and recommended by one of the principals, accurate to } \sim 40\% \text{ (Ballinger 1993, Ballinger 2005).}$$

$$\text{ARF} = 5.121 \times 10^{-6}$$

This should correspond closely to recent testing for a dynamic situation (PNNL 2004) if spill heights are ratioed accordingly using the reference z 's (e.g., $(z_2/z_1)^3$).

Account for deposition of the mean particle. This is the same as the bubble diameter found previously and guessing a particle density:

$$D_m := D_B \quad \rho_p := 1.4 \frac{\text{kg}}{\text{L}}$$

The settling velocity is (assuming the Cunningham-Stokes factor is 1):

$$v_{\text{set}} := \frac{\rho_p \cdot D_m^2 \cdot g}{18 \cdot \mu_g} \quad v_{\text{set}} = 0.011 \frac{\text{m}}{\text{s}}$$

The particles deposited are (Ballinger 1993):

$$d := 1 - \exp\left(\frac{-v_{\text{set}}}{v_g}\right) \quad d = 0.98$$

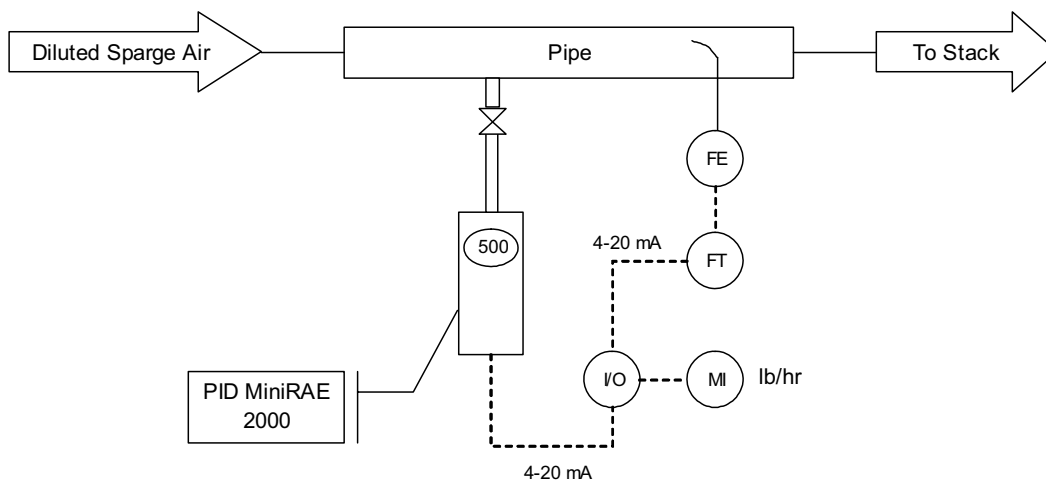
Note: the distance to the filter and spill distance were equal in this equation and therefore cancelled out.

Since 98% deposit, there is little splash entrainment.

The gas concentrations are then the emission rates/sparge rate and use 40 cfm for worse-case.

IV. VOC Analyzer

A photoionization detector (PID) will be used in conjunction with a flowmeter to provide a rate in lb/hr of VOCs. The problem is that the analyzer is calibrated in terms of isobutylene and needs correction to a mixture of gases. Humidity also requires a correction factor. The PID comes with different lamp energies with higher energies being able to ionize VOCs with higher ionization potentials. The schematic below shows the instrument arrangement followed by a typical vendor web page that shows where the data comes from. The integrator takes signals from the PID and flowmeter and multiplies them together and an external factor determined below in a simplified version.



http://www.raesystems.com/~raedocs/App_Tech_Notes/Tech_Notes/TN-106_Correction_Factors.pdf

The 11.7 eV lamp can analyze all of the VOCs expected. However, it doesn't last long and requires frequent calibration. Therefore, the 10.6 eV lamp will be used. The 10.6 eV lamp is recommended by the vendor but it is limited in the number of VOCs, especially TCA that has a large impact on the mixture correction factor if it is in much larger quantities than expected.

The table below provides the gases estimated from the recent operation determined from the FTIR for all operations (Tyson 2005). This is an approximation of what will be seen in current sparging efforts. Some corrections may be required using FTIR data to adjust mole fractions.

VOC	Formula	Total mol	mol%	Renorm	10.6 eV CF	mol%/CF	11.7 eV CF*	mol%/CF
Carbon Tetrachloride	CCl_4	0.27	0.13%		NR		1.7	0.00
Chloroform	CHCl_3	9.05	4.21%		NR		3.5	0.01
Dichloromethane	CH_2Cl_2	0.09	0.04%		NR		0.89	0.00
Chloromethane	CH_3Cl	4.11	1.91%		NR		0.89	0.02
Perchloroethene	C_2Cl_4	19.56	9.08%	11.55%	0.57	0.20	0.31	0.29
Trichloroethene	C_2HCl_3	143.87	66.81%	84.99%	0.54	1.57	0.43	1.55
cis-1,2-Dichloroethene	$\text{C}_2\text{H}_2\text{Cl}_2$	0.16	0.08%	0.10%	0.8	0.00	0.78	0.00
1,1-Dichloroethene	$\text{C}_2\text{H}_2\text{Cl}_2$	3.19	1.48%	1.89%	0.82	0.02	0.8	0.02
Vinyl Chloride	$\text{C}_2\text{H}_3\text{Cl}$	2.49	1.16%	1.47%	2	0.01	0.6	0.02
1,1,1-Trichloroethane	$\text{C}_2\text{H}_3\text{Cl}_3$	27.94	12.97%		NR		1	0.13
1,1-Dichloroethane	$\text{C}_2\text{H}_4\text{Cl}_2$	0.19	0.09%		NR		0.6	0.00
1,2-Dichloroethane	$\text{C}_2\text{H}_4\text{Cl}_2$	4.30	2.00%		NR		0.6	0.03
Chloroethane	$\text{C}_2\text{H}_5\text{Cl}$	0.10	0.05%		NR		1.1	0.00
		215.34	100.00%		Cfmix	0.55	Cfmix	0.53
			78.61%	100.00%				

*No value for chloromethane. Use NR for 10.6 eV and DCM for 11.7eV. Only had 1 value at 10.6 for Cis-1,2-DCE went down by 0.02 to match 1,1-DCM. No value for 1,1-DCE, used NR 10.6, 0.6 11.7.

The individual correction factors (CFs) listed were provided by RAE systems (RAE 2005) as shown in the table under the lamp power. The mixture CF was found using the individuals in the table by:

$$\text{CF}_{\text{mix}} = \frac{1}{\sum_{i=1}^n \frac{y_i}{\text{CF}_i}} \quad \text{Where: } y_i = \text{mol fraction and } \text{CF}_i = \text{individual correction factor}$$

The mixture CFs are shown in the table for both lamps and are surprisingly close. The method is to assign a mole rate as a basis, then calculate mass rates based on what is seen by both lamps. This will provide an additional factor that will be used in the "exterior factor" (note exterior factors are input into the integrator (shown as I/O in diagram) whereas the mix CF x humidity CF is input into the PID). This is f_G and is the mass rate by 11.7 eV/mass rate by 10.6 eV. This factor will not change regardless of the actual mole rate for the mole fractions in the table. Note that renorm in the table recalculates the mole fractions based on what is seen by the 10.6 eV lamp. The following table is the result of this and provides an exterior factor.

Basis, mole/hr	1			
	mole/hr	ppm	mol/hr	ppm
CCl ₄	1.25E-03	17		
CHCl ₃	4.21E-02	559		
CH ₂ Cl ₂	3.99E-04	5		
CH ₃ Cl	1.91E-02	254	1.91E-02	254
C ₂ Cl ₄	9.08E-02	1208	9.08E-02	1208
C ₂ HCl ₃	6.68E-01	8884	6.68E-01	8884
C ₂ H ₂ Cl ₂	7.60E-04	10	7.60E-04	10
C ₂ H ₂ Cl ₂	1.48E-02	197	1.48E-02	197
C ₂ H ₃ Cl	1.16E-02	154	1.16E-02	154
C ₂ H ₃ Cl ₃	1.30E-01	1725		
C ₂ H ₄ Cl ₂	8.78E-04	12		
C ₂ H ₄ Cl ₂	2.00E-02	265		
C ₂ H ₅ Cl	4.83E-04	6		
Total	1.00E+00	13296	8.05E-01	10707
	MWave	131	MWave	134
Reading on 11.7 eV	25072	Reading on 10.6 eV	19359	
g/hr by 11.7 eV	7.64E-03	g/hr by 10.6 eV	6.02E-03	
Exterior Factor	1.27			

From the table, the exterior factor is: $f_G := 1.27$

Humidity also requires correction. However, it is normally low and will keep at one unless humidity is consistently high. The figure below provides the adjustment if the humidity increases above that expected.

$$C_H := 1.0 \quad C_{F_{mix}} := 0.55 \quad MW_{ave} := 134 \frac{\text{gm}}{\text{mol}}$$

The combined correction interior correction factor to input into the PID is:

$$C_{comb} := C_{F_{mix}} C_H \quad C_{comb} = 0.55$$

This correction factor is entered into the MiniRae 2000 so that the output is in ppm_v of the VOCs in the 10.6 eV columns, i.e., at a reading of 1000 as isobutylene (no CFs), it will be:

$$\begin{aligned} \text{PCE} &:= 0.55 \cdot 1000 \text{ppm}_v \cdot 0.12 & \text{PCE} &= 66 \text{ppm}_v \\ \text{TCE} &:= 0.55 \cdot 1000 \text{ppm}_v \cdot 0.85 & \text{TCE} &= 467.5 \text{ppm}_v & \text{ETC.} \end{aligned}$$

However with the CF input into the PID, it would be:

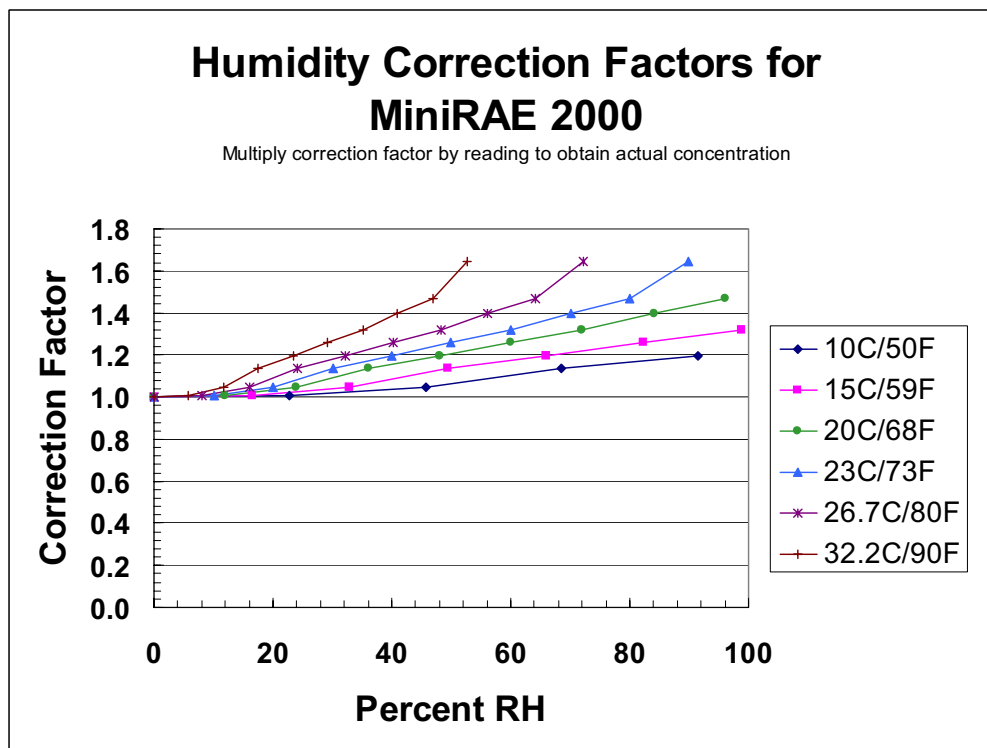
$$\text{PCE} := 1000 \text{ ppm}_V \cdot 0.12$$

$$\text{PCE} = 120 \text{ ppm}_V$$

$$\text{TCE} := 1000 \text{ ppm}_V \cdot 0.85$$

$$\text{TCE} = 850 \text{ ppm}_V$$

ETC.



Integrated flow to obtain lb VOC/hr after CF_{comb} entered. This factor (f_I) is input into the integrator (as a multiplying operator):

$$r_{\text{VOC}} = \frac{Y_{\text{PID}} \cdot Q \cdot \text{MW}_{\text{AVE}}}{R_{\text{star}}} = Y_{\text{PID}}(\text{ppm}_V) \cdot Q(\text{scfm}) \cdot f_I$$

The exterior factor to enter into the integrator is:

$$f_I := \frac{\text{MW}_{\text{ave}}}{359 \frac{\text{ft}^3}{\text{lbmol}} \cdot 10^6} \cdot 60 \frac{\text{min}}{\text{hr}} \cdot f_G \quad f_I = 2.847 \times 10^{-5} \frac{\text{lb} \cdot \text{min}}{\text{ft}^3 \cdot \text{hr}}$$

Note: MathCad calculations will not have 10^6 for f_I .